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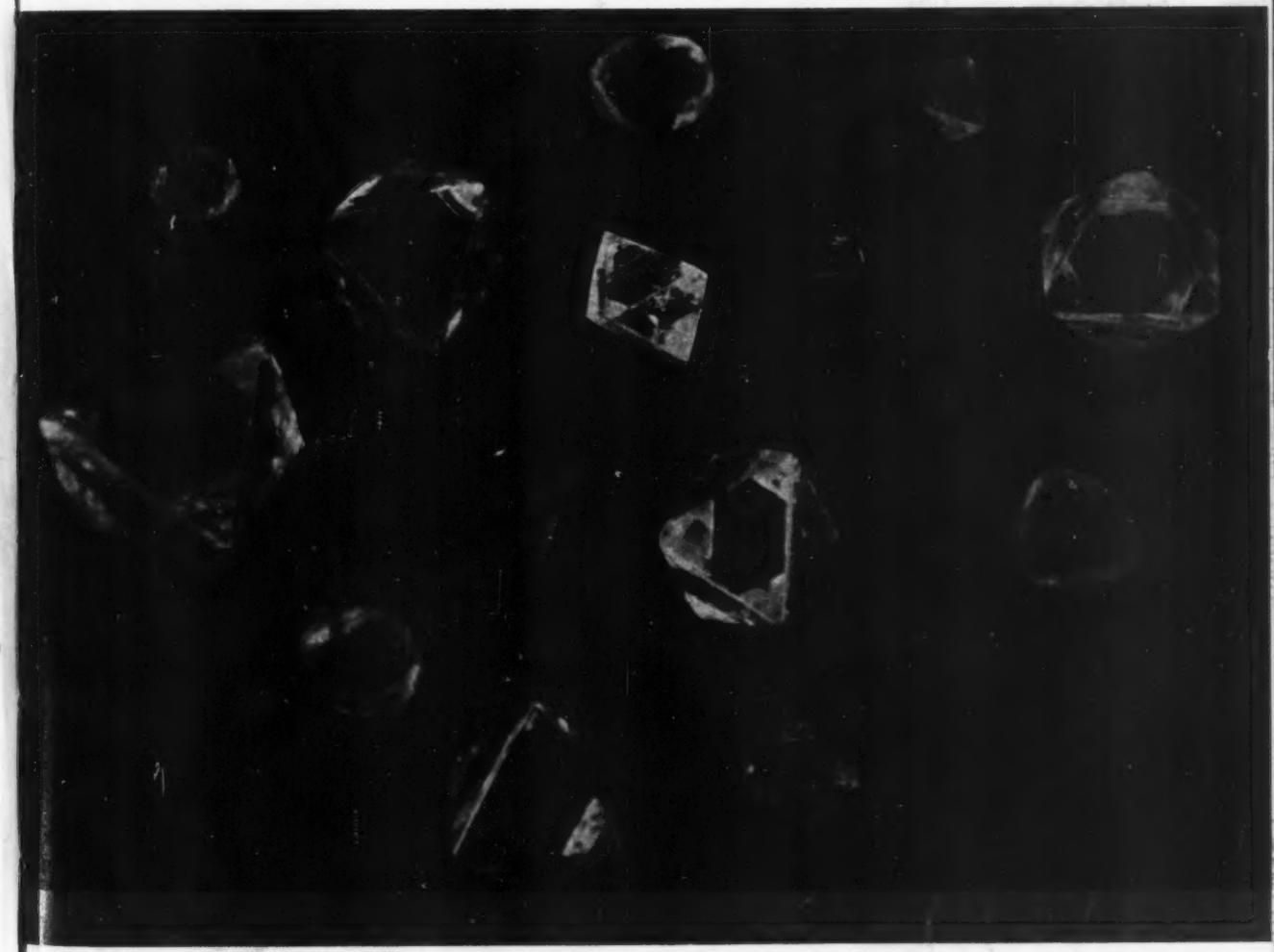

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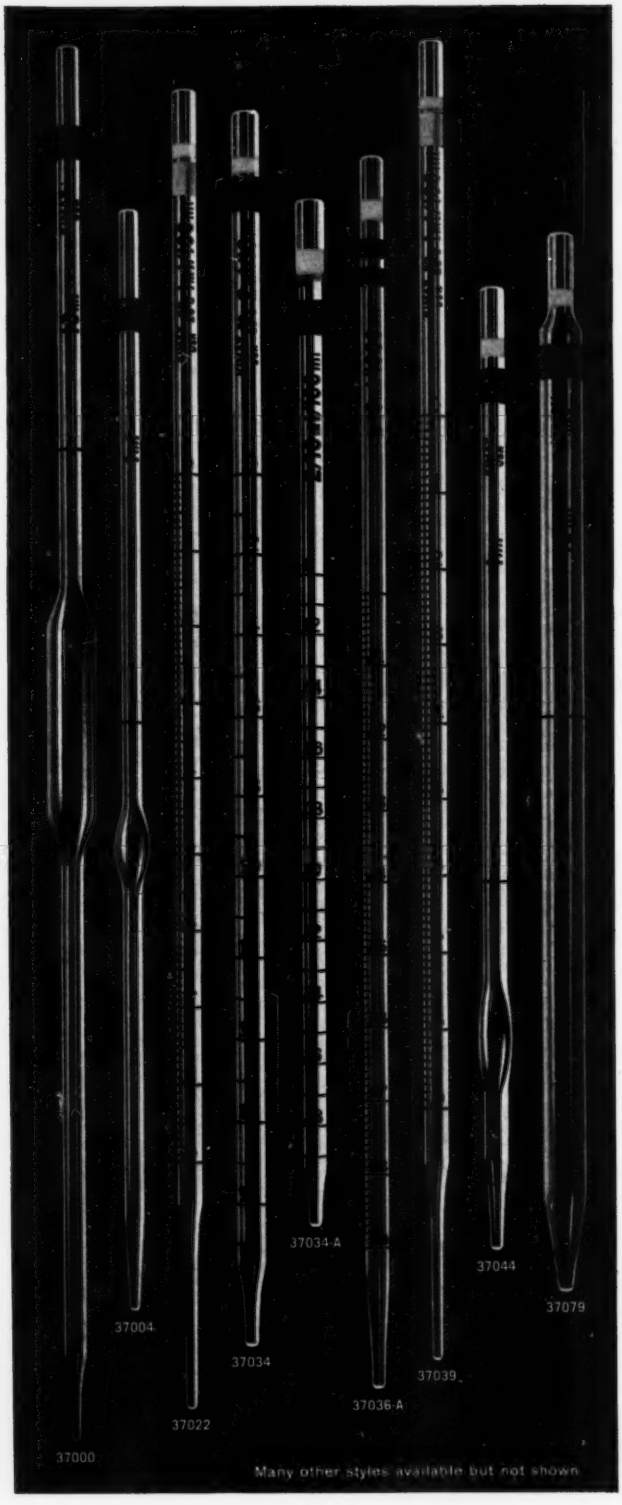

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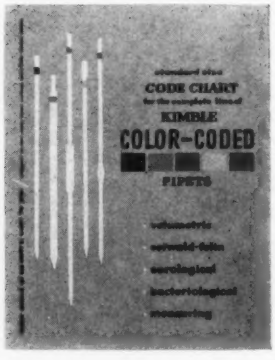

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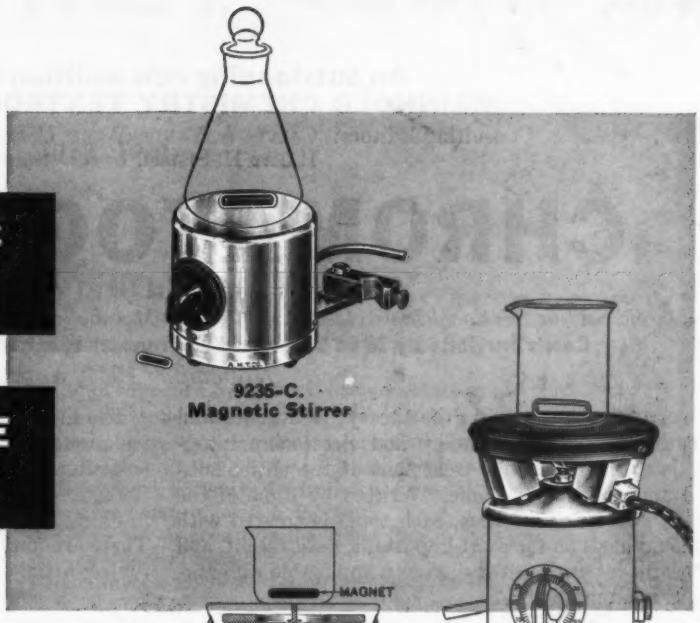

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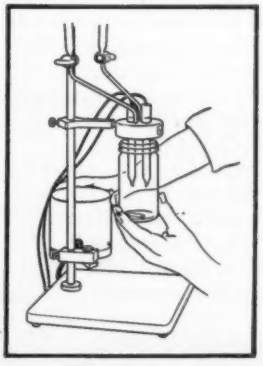

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CHROMATOGRAPHY

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The book will be of special value not only to chemistry teachers and students at the undergraduate and graduate levels, but to almost all chemists and allied professions. It thoroughly presents the most efficient methods of separation used in organic, inorganic, industrial, and biological chemistry.

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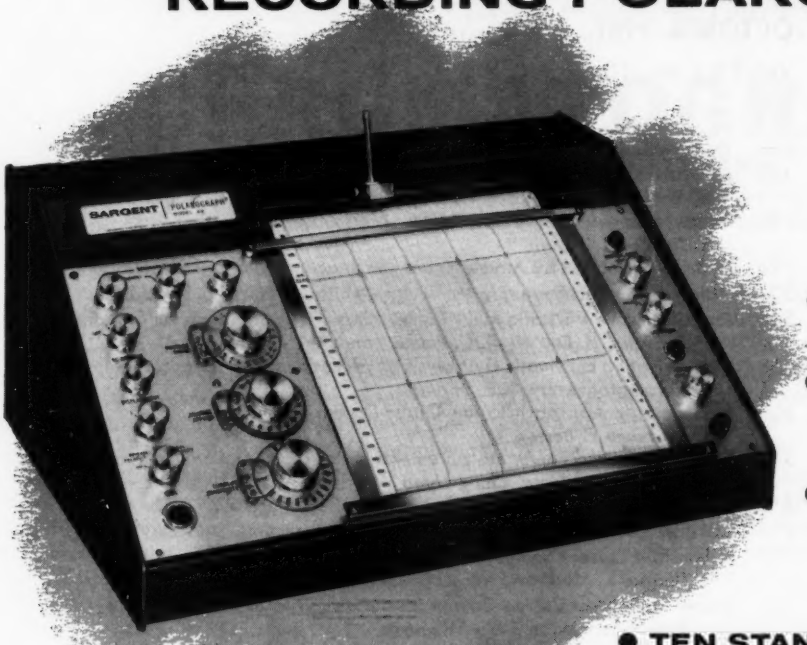

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This series of articles presents a survey of the basic principles, characteristics, and limitations of those instruments which find important applications in chemical work. The emphasis is on commercially available equipment, and approximate prices are quoted to show the order of magnitude of cost of the various types of design and construction.

14. Chromatographic Equipment (Continued)

The application of an electric potential to a solution containing dissolved or suspended particles which interact with (i.e., feel a force due to) the field is a general technique for producing directed migration of those particles. The term *ionophoresis* was originally coined to refer to the movement of small inorganic ions under the influence of an electric field, and *electrophoresis* was later defined as designating the analogous motion of colloidal particles. If the conditions in the fluid are so arranged that a zone, interface or boundary layer is initially formed by the specimen in the liquid medium, and if there are present in the specimen particles having different mobilities, the application of the electric field causes each type of particle to migrate at a characteristic rate, and a set of more-or-less distinguishable zones is formed. The resolution of a mixture into its components in this manner is called *zone electrophoresis*. There are two types of zone electrophoresis; the classical, free liquid technique, and the stabilized medium technique.

The classical technique involves differential electromigration in a free (i.e., unstabilized) liquid. In order to achieve effective separations by this technique, great care must be taken to eliminate the effects of mechanical vibration, agitation, or convective disturbances. Even with these factors under control, free liquid zone electrophoresis is generally successful only with high molecular weight samples, since the random diffusional processes which oppose the directed migration and smear out the electrophoretic pattern are faster, the smaller the migrating species.

The substitution of a stabilized medium for the free liquid has produced a significant advance in technique, for it has made possible many types of quick analyses and separations with simple, inexpensive, and efficient equipment. The types of stabilized media which have been employed include: liquid supported on paper, liquid held by capillary forces in packed columns of cellulose powder, liquid supported on glass powder or beads, agar gel, silica gel, starch gel, and polyacrylamide gel.

Electromigration in one of these stabilized media is often a much more complex mechanism than free electrophoresis, for it involves adsorption and partition effects superimposed upon the electric field effects. Hence, the terms paper (or starch, or agar, etc.) electrophoresis, which are widely used, have been criticized because they do not emphasize the important roles which may be played by adsorption and partition. Consequently, the term *electrochromatography* has been proposed to cover all types of electrophoretic techniques in stabilized media. Some authors prefer to use *pherography* to denote these techniques.

Design Considerations for Stabilized Medium Pherographs

When a voltage is applied across a length of one of the stabilized liquid media described above, the ensuing flow of current produces the following effects: (*1*) electromigration of charged particles in the direction of the oppositely charged electrode; (*2*) heating of the migration track, which results in evaporation of liquid and a consequent flow of liquid from the wetter to the dryer regions, and (*3*) endosmotic flow of the liquid in the direction of one of the electrodes.

In the case of most of the supporting phases used in electrophoretic work, the solid tends to acquire a negative charge when it is in contact with an aqueous solution containing an electrolyte. When a potential is applied, this charge causes the supporting phase to want to migrate toward the anode. Since it is rigid and cannot so migrate, the same relative motion is produced by a streaming of the liquid phase in the opposite direction, i.e., toward the cathode. This electroosmotic flow is greatest in ground glass, and decreases in the order agar > starch > paper. On paper, the rate of streaming increases with increasing pH.

These factors impose a practical limitation on the length of the migration path for which an instrument of this type can be designed. If the linear distance between the ends of the migration path is too large, the passage of current may dry out the central part of the supported medium faster than liquid can flow to it from the buffer reservoirs at the ends. Even with short path instruments, there is a considerable buffer flow from both ends toward the center of the migration path. The net result is a non-uniform rate of fluid flow as a function of distance along the path, as indicated schematically in Figure 34. As a migrating component moves along, it may find itself traveling against the current of buffer flow arising from factors (*2*) and (*3*) above. When it reaches a place where its migration velocity is equal and opposite to the rate of flow of the medium, it no longer advances, and nothing is gained by lengthening the migration path or prolonging the time of electrophoresis.

In general, the mobility of an ion is inversely proportional to the square root of the ionic strength of the solution. Hence, the rate of electrophoresis can be speeded up by working in solutions of low ionic strength. However, reduction in the ionic strength causes the resistance of the medium to increase, and in order to gain in speed of migration, it is necessary to increase the applied voltage in proportion to the rise in resistance.

The energy dissipated per unit time in the medium due to the flow of current is:

$$P = E^2/R = E \times I$$

If R is constant, as in the case of a medium of constant ionic strength, the power increases as the square of the applied voltage. If I is constant, as in the case where the applied voltage is adjusted to offset increases in R, the power increases linearly with the applied voltage. The practical limitation to the amount of power input that can be tolerated is the efficiency of cooling of the migration path by gas convection, evaporation, and/or a cold table support for the medium.

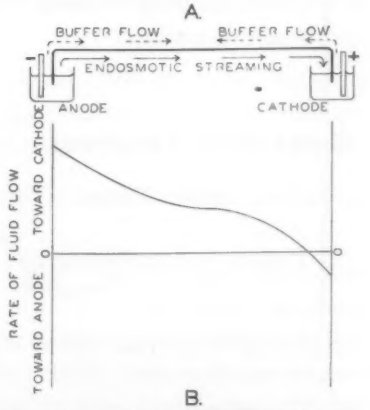
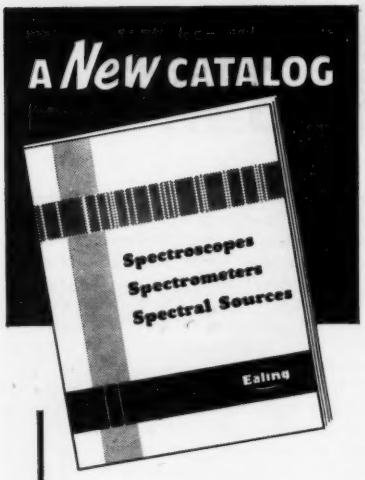


Figure 34A. During electrophoresis with a supported liquid, the buffer streams across the support as a consequence of endosmosis plus the effect of evaporation from the central portion of the migration path.
B. The net flow of liquid is not uniform from one end of the path to the other.

Each zone in an electrophoretogram (pherogram) tends to spread out due to thermal diffusion. At a given temperature, this spreading is proportional to the square root of the time. Hence, an electrophoresis run should be completed in as



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short a time as possible. In some cases the best separations are achieved by applying a high potential to the stabilized medium, in order to produce rapid migration, and employing a non-aqueous liquid (such as toluene) in direct contact with the medium to remove the thermal energy and keep the migration path from drying out.

The use of a supporting medium for the liquid phase through which the charged particles migrate makes it possible to base the separation of certain substances upon differences in the bulk of the particles. Thus, in the case of the various gels, the migrating particles must pass through the pores in the gel structure, and these pore sizes are characteristic of the type of gel involved. For this reason, e.g., starch gel electrophoresis will resolve certain samples into more zones than are observed with the same sample subjected to paper electrophoresis. In the case of the gel, molecular sieving aids the separation process.

Specialized Types of Pherographs

High voltage electrophoresis tanks and power supplies are manufactured by Servonuclear Corp., Long Island City 2, New York. The tanks are designed to provide efficient cooling either by means of a center partition with imbedded cooling coils (Model ET 24 Large Tank Paper Electrophoresis Fingerprint Apparatus, Lucite construction, accommodates 18- × 22-inch paper sheets on a vertical frame, $595), or by cooling coils imbedded in the sides of the tank (Model ET48, stainless steel coils, Lucite construction, accommodates 22- × 48-inch paper sheets on a vertical frame, $700). The power supplies available include a unit that can provide up to 5000 volts dc at currents up to 300 milliamperes (Model EHV 5000, $795).

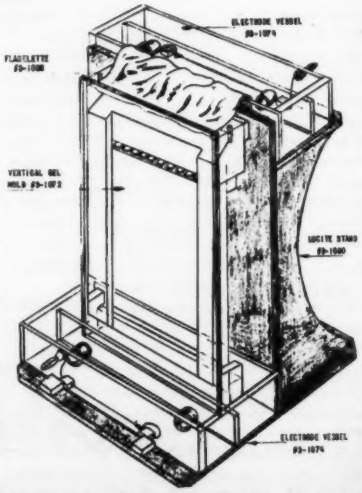

Figure 35. Design of the vertical starch gel electrophoresis assembly made by Buchler Instruments, Inc.

A starch gel vertical electrophoresis

(*Continued on page A716*)

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apparatus is available from Buchler Instruments, Inc., New York 31, N. Y. (Model 3-1070, without power supply, $190). The assembly, shown in Figure 35, consists of a vertical Lucite stand, a gel mold, and two electrode buffer chambers. Two shelves, one on the base, the other on the top of the vertical stand, extend in opposite directions and offer support for the two electrode buffer chambers. The gel mold stands in the lower chamber, which is filled with buffer solution. The ionic flow to the top electrode is established by means of a piece of flannelette which serves as a wick between the top of the gel column and the upper buffer chamber. A comb assembly with 10 prongs is mounted at the underside of the gel block, and permits 10 samples of 0.040 to 0.045 ml each to be introduced. A special constant current power supply which regulates the output current within ±0.5% at any value up to 200 ma at voltages up to 1000 v is available for use with the starch gel apparatus (Model 3-1014, $362).

An instrument designed for microelectrophoresis and specialized immunological tests with agar-coated plates is made by National Instrument Laboratories, Inc., Washington 18, D. C. Microscope slides are coated with a thin film of agar, and placed on a support frame. Filter paper wicks make contact from the ends of the slides to the electrode buffer compartments. One unique feature of this equipment is the provision of a pair of voltage probes which touch the agar-coated slides near their ends and permit the operator to measure the actual potential existing across the migration path during the run. Another feature is the special pattern in which the gel is cut for immunological studies. First, two small holes are cut out, and the samples of antigen solution to be tested are added to the cavities. The components of the samples are caused to

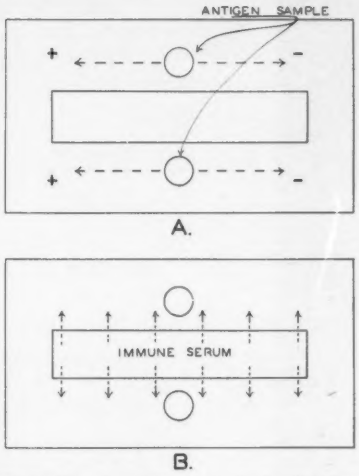


Figure 36. A. Antigen sample is placed in the small circular holes and is subjected to electrophoresis to spread out the components. B. Immune serum is then placed in the channel, and allowed to diffuse into the electrophoretic pattern.

migrate by applying the electric field in the direction of the long axis of the slide, as shown in Figure 36A. The slide is then removed from the pherograph and the long, narrow channel of agar is removed. The reagent, a solution of immune serum, is pipetted into this channel, and allowed to diffuse outward into the path of the electrophoretic pattern, as indicated in Figure 36B. Wherever an antigen and antibody meet, precipitation occurs, and after the addition of a suitable dye, a characteristic pattern is obtained, as shown in Figure 37. It is probable that this technique may be useful in the identification and estimation of other substances than proteins by suitable choice of the reactants.

Electrophoresis in short cylindrical columns of polyacrylamide gel is possible

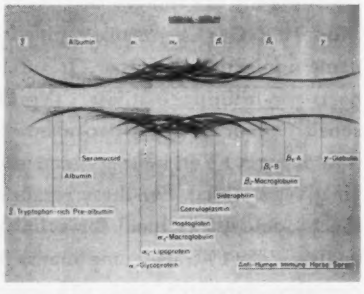
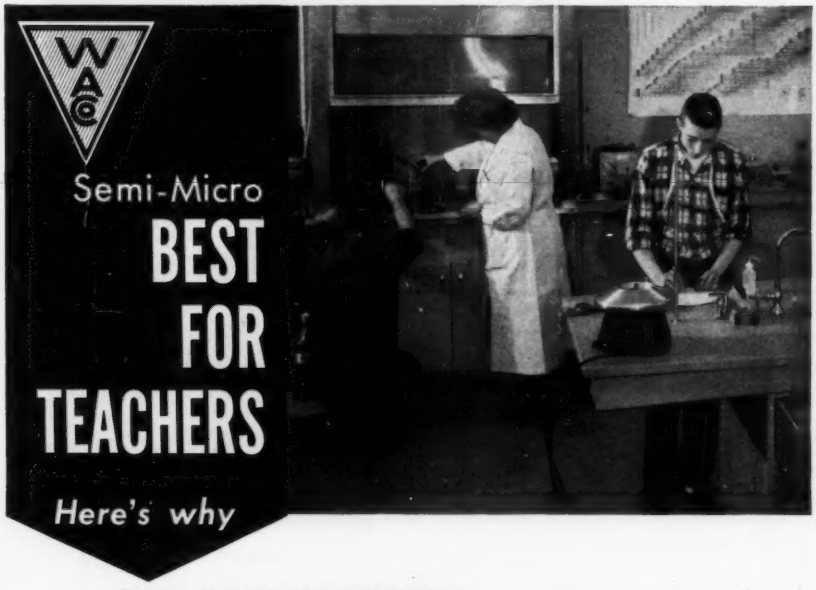


Figure 37. A typical precipitation pattern resulting from the reaction between antigen and antibody as carried out by the technique illustrated in Figure 36.

with the Disc Electrophoresis equipment available from Canal Industrial Corp., Bethesda 14, Maryland (Model 12, $450). An open-ended glass tube, 5 mm id × 70 mm long, is stoppered at one end, and is

(Continued on page A718)



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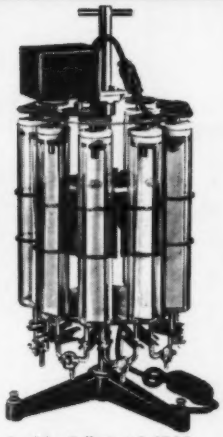

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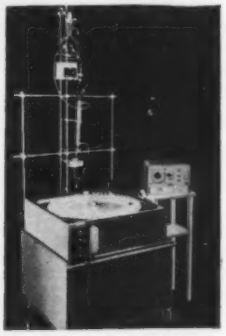

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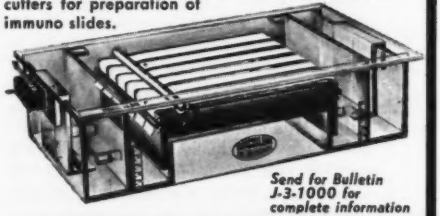

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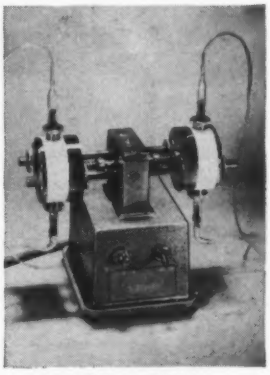

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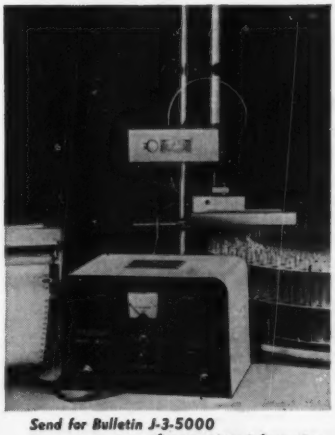

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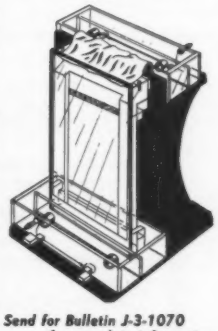

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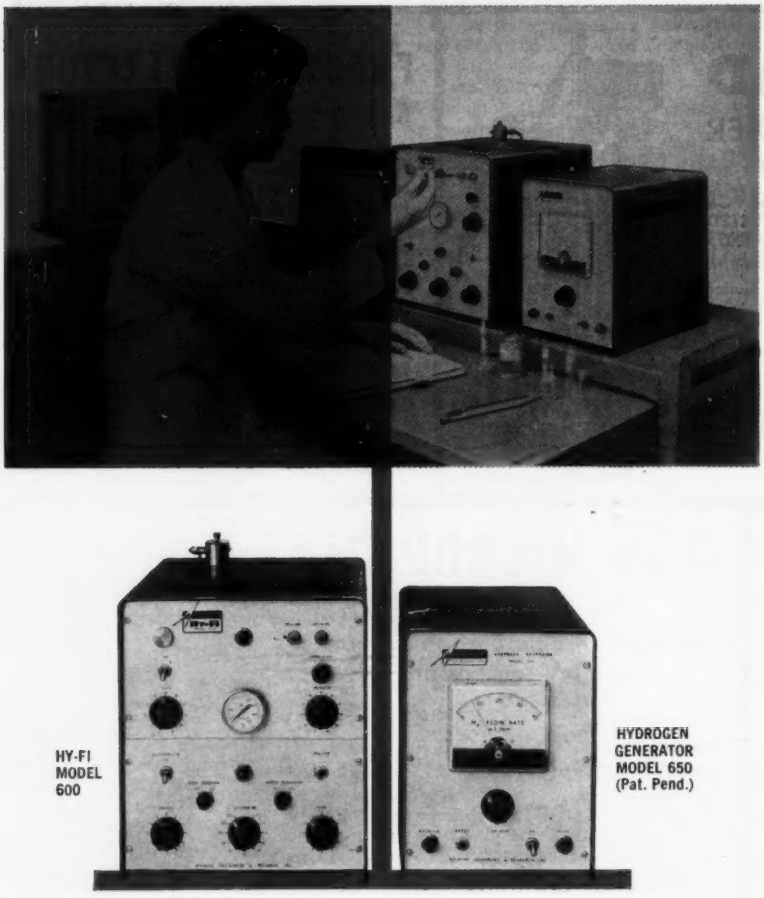

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Continuous Flow Electrochromatographs

In the chromatographic and electrophoretic techniques discussed to this point, all the forces operating to produce the differential migration have acted along a common axis, as illustrated in Figure 38. However, the use of an electric potential as a source of motive power permits an extra degree of freedom in the relative disposition of these force vectors, for the lines of electric force can be easily oriented in any desired direction by suitable placement of the electrodes. If the electric force is directed at right angles to the axis of fluid flow due to capillarity and gravity, as shown in Figure 38F, the resultant motion of the migrating species will be at some angle between 0 and 90°, the exact angle being determined by the relative magnitudes of the mobilities of the species under the influence of the different forces.

This result lends itself admirably to the design of preparative-scale chromatographs. Figure 39 shows a schematic diagram of the principle of a paper curtain continuous flow electrochromatograph. The paper sheet is mounted as for descending chromatography, and the background electrolyte or buffer solution flows down the sheet, causing any sample components on the paper to migrate downward. At the same time, an electric field is applied horizontally across the paper sheet by means of end tabs which dip into electrode compartments. Consequently, the sample components migrating downward under the influence of the descending liquid medium are caused to acquire a component of drift in the direction of one of the electrodes. At the bottom of the sheet a series of serrated edges, or drip tips, directs the fluid into a row of receiving tubes. Thus, sample components of different chromatographic and electrophoretic properties will be washed off the paper at different places and will be collected in different tubes.

With this arrangement, a sample solution may be added at a uniform rate at a

(*Continued on page A720*)

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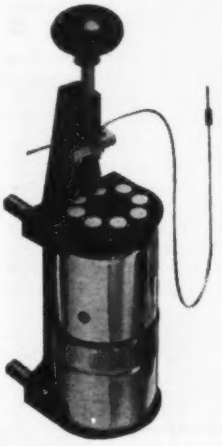

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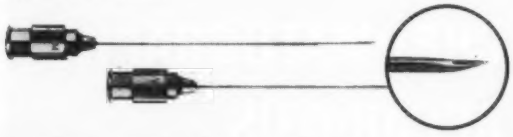

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given point near the top of the sheet, through a wick or other means, and the fractionated components may be collected continuously at the bottom. A run may be continued for many days, and as much as several grams of sample may be fractionated before the paper sheet deteriorates enough to require replacement.

In order to maintain a constant separation pattern on the paper, so that the advantages of the continuous flow electrochromatographic technique can be fully realized, attention must be paid to the following design considerations. (*1*) The rate of flow of electrolyte down the paper must be held constant. This requires that the level of the liquid in the upper feed reservoir, i.e., the hydrostatic head, be kept constant. (*2*) The conductivity of the electrolyte must remain constant, so that the potential field and current flow across the paper will not vary. If prolonged runs are to be made, means should be provided for preventing the electrolysis products formed around the electrodes from reaching the paper or the electrolyte reservoir. (*3*) The potential and current should be supplied by a regulated power supply, and the output of this device should be free of appreciable ac ripple,

(*Continued on page A722*)

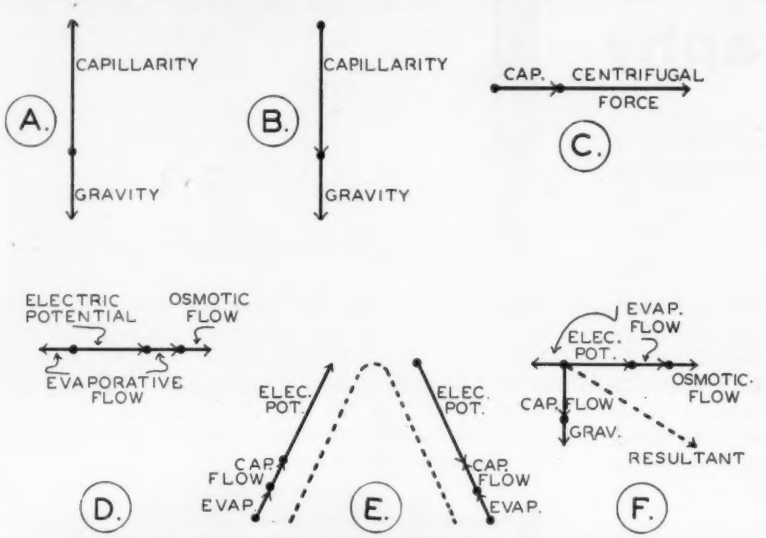

Figure 38. Vector diagrams showing the directions of the forces involved in the various chromatographic and electrophoretic techniques. A. Ascending chromatography. B. Descending chromatography. C. Centrifugally-accelerated chromatography. D. Flat-bed electrophoresis. E. Ridge-pole electrophoresis. F. Continuous flow electrophoresis.

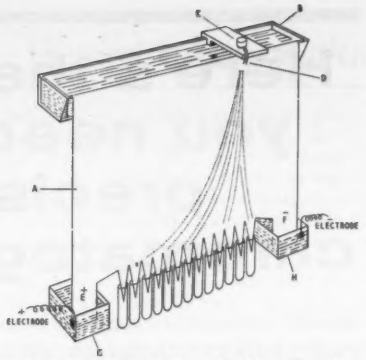

Figure 39. Illustrating the principle of hanging paper curtain continuous flow electrophoresis. A. Paper sheet. B. Solvent trough. C. Sample. D. Wick. E, F. Tabs dipping into electrode compartments. G, H. Electrode compartments. ■

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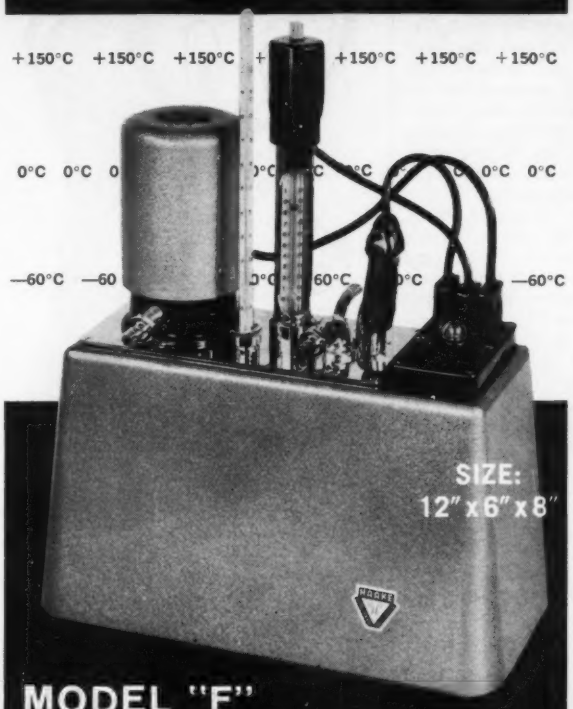

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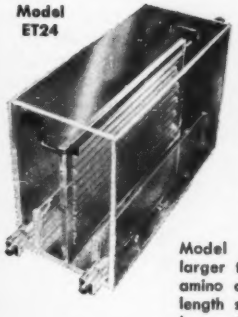

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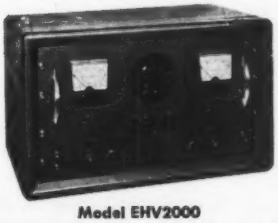

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which produces undesirable heating effects. (4) The sample should have the same pH and conductivity as the background electrolyte, and should be fed onto the paper sheet at a constant and uniform rate. Several continuous flow electrochromatographs are at present commercially available, and these vary in elaborateness, price, and mechanical complexity in proportion to the manner in which the above design factors are taken into account.

Shandon Scientific Company Ltd., London S.W. 7, England, manufactures a continuous flow apparatus of the type described above (No. 2520 Continuous Electrophoresis Apparatus, about $250; U.S. distributor, Consolidated Laboratories, Inc., Chicago Heights, Illinois). The electric field may be applied to the paper sheet by means of the wick arrangement shown in Figure 39, or by means of a pair of side electrodes that clamp onto the vertical edges of the sheet, as illustrated in Figure 40. The latter produces a more uniform electric field across the paper sheet. The electrodes consist of platinum wires mounted in cellophane tubes which are held against the paper sheet by plastic clamps. The buffer solution flows continuously through the cellophane tubes, so

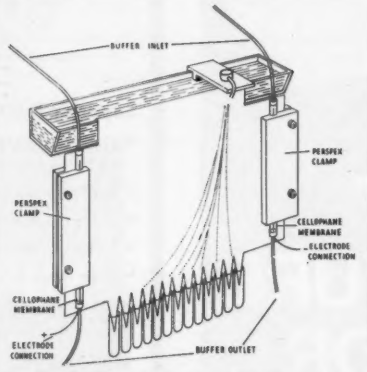
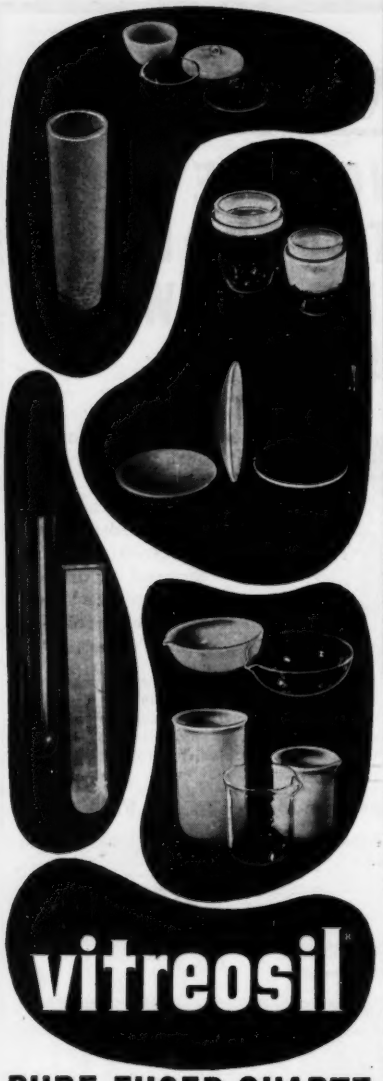


Figure 40. Side electrode contactors, as employed in the Shandon continuous flow electrophoresis apparatus.

that electrolytic contact is made with the paper, and electrolysis products formed around the electrodes are washed away. The apparatus can accommodate paper sheets 18 × 22 inches or smaller, down to 10 × 13 inches. A shelf at the rear top of the apparatus holds a 2-liter buffer stock bottle, from which a constant hydrostatic head feed delivers the solution to the paper trough. The excess buffer from the lower compartments is collected in overflow bottles at the base, and may be discarded or returned by the operator to the buffer storage bottle.

The design of the continuous flow paper electrophoresis apparatus made by Spinco Division of Beckman Instruments, Inc., Belmont, California, is shown in Figure 41 (Model CP, $1550, without power supply). The electrolyte feed level in the upper trough is maintained constant by means of a pump which either continually adds fresh solution to this trough, or recirculates the overflow from the electrode compartments,

(*Continued on page A724*)



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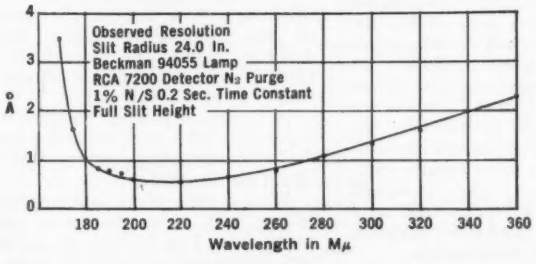

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if desired. Electrical contact is made along the vertical edges of the paper curtain by means of two stacks of filter paper wicks which are kept saturated with the electrolyte through a controlled overflow from the paper trough. The sample is

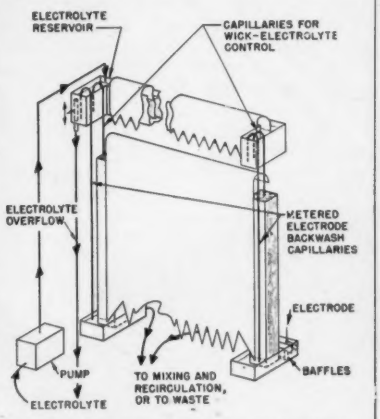


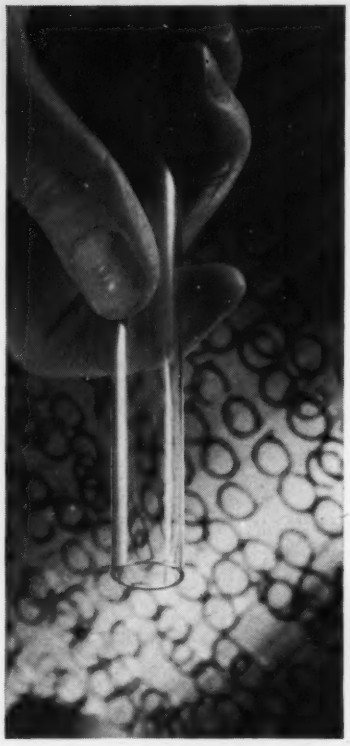
Figure 41. Design of the Spinco Model CP continuous flow apparatus.

added to a wick near the top of the paper sheet by gravity flow from a sample reservoir. The height of this reservoir is decreased during a run by means of a motor control at such a rate as to maintain a constant feed-rate onto the paper. Constant current power supplies are available for use with this apparatus (e.g., Model Constat, 10–100 ma at 1000 v, current regulation ±2%, $360).

Microchemical Specialties Co., Berkeley 10, California, manufactures several models of this type of instrument which they call "Spectrolators." One is a large, preparative-scale apparatus, capable of handling up to one liter of sample per day (Misco Spectrolator, about $7500). It contains a 1-hp refrigeration unit for cooling an air stream to about 1°C; this cold air is then directed across both sides of the paper curtain to remove the heat generated by the applied voltage. When a run is complete, the refrigeration cycle can be reversed to make a stream of hot air available for rapid drying of the curtain while in the apparatus. A 5000-v dc power supply is provided, and with its use voltage gradients as high as 110 v/cm can be obtained. Sample is fed onto the curtain by means of a positive displacement feed device that has a variable volumetric adjustment and refills automatically. Buffer fluid is maintained at a constant hydrostatic head and is added or circulated by a motor-driven pump.

This manufacturer also produces the smallest version of a continuous flow electrochromatograph (Kirk-Misco Variable Angle Plate Spectrolator, about $200). This unit, shown in Figure 42, weighs only 3.75 lb complete with power supply. The paper sheet rests on a Plexiglas table support which can be adjusted to be horizontal, or to make angles of 9, 16, or 27° with the horizontal. This permits the operator to seek the optimum rate of

(*Continued on page A726*)



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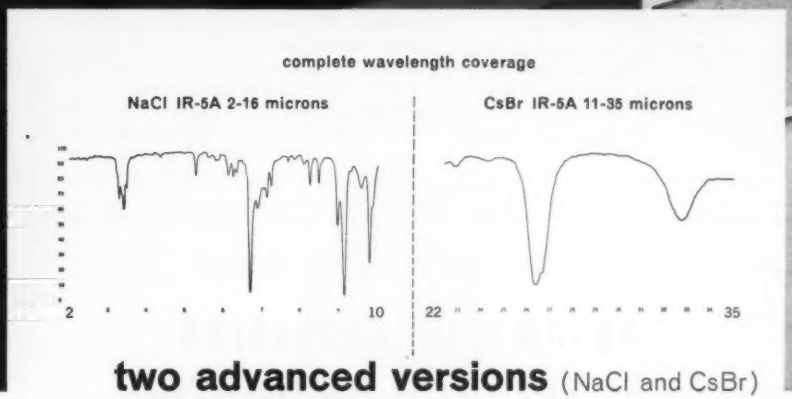

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flow of the background electrolyte down the paper. The power supply output is 0–350 v, 0–15 ma. The apparatus can be used either for chromatography or electrophoresis with microgram or microliter size specimens, or it can be used in continuous flow to process milligrams of sample in 24-hour or longer periods. The collecting tubes hold a total of less than 8 ml. The feeder reservoirs have no provision for the maintenance of a constant level, since the fall in level during the filling of the collection tubes is not large.

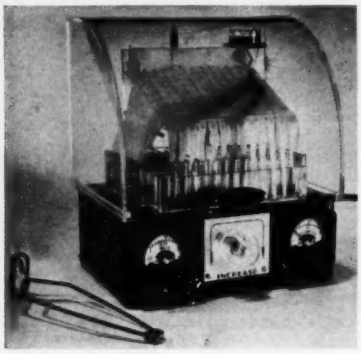

Figure 42. The Kirk-Misco Variable Angle Plate Spectrolator, smallest of the commercial instruments for continuous flow electrophoresis.

An apparatus for large-scale continuous flow electrophoresis in which a bed of glass microbeads provides the stabilization of the fluid phase is manufactured by the JKM Instrument Co., Durham, Pennsylvania (JKM-Stubbings Continuous Electrophoresis Apparatus, complete with power supply, $3180). The electrophoresis cell consists of a pair of 0.5-inch Lucite plates cemented and clamped in position with a 0.5-inch spacing between them. This space is filled with a uniform packing of Pyrex microbeads. For buffer flow rates of 1 to 3 liters per hour, the glass beads are between 100 and 140 mesh (105 to 149 microns diameter); for 0.5 to 1 liter/hour, 74–105 micron beads are employed; and for 0.25–0.5 liter/hour, the bed is made up of 63–88 micron diameter beads.

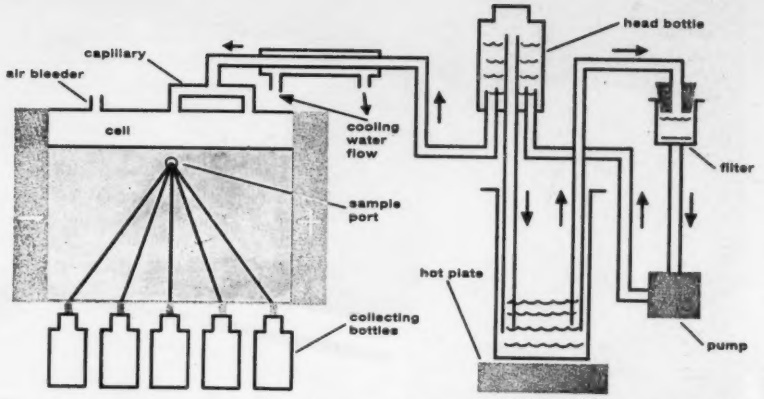

Figure 43. Schematic representation of the buffer feed system employed in the JKM-Stubbings continuous Electrophoresis Apparatus. The main buffer reservoir is on the hot plate where dissolved air is removed; buffer is pumped through the filter and to the head bottle, thence through the cooling condenser and into the electrophoresis cell.

The arrangement employed for circulation of the buffer solution is shown schematically in Figure 43. A 4-liter reservoir is maintained at the base of the instrument. This solution is kept at 50–55°C by an adjustable, thermostated hot plate. This expels any dissolved air, which would otherwise form bubbles in the bed of beads and lead to uneven flow. An automatic pump draws buffer from the reservoir

(*Continued on page A730*)

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Readability of Dial: .02 grams

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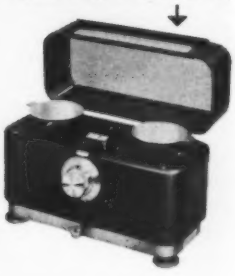

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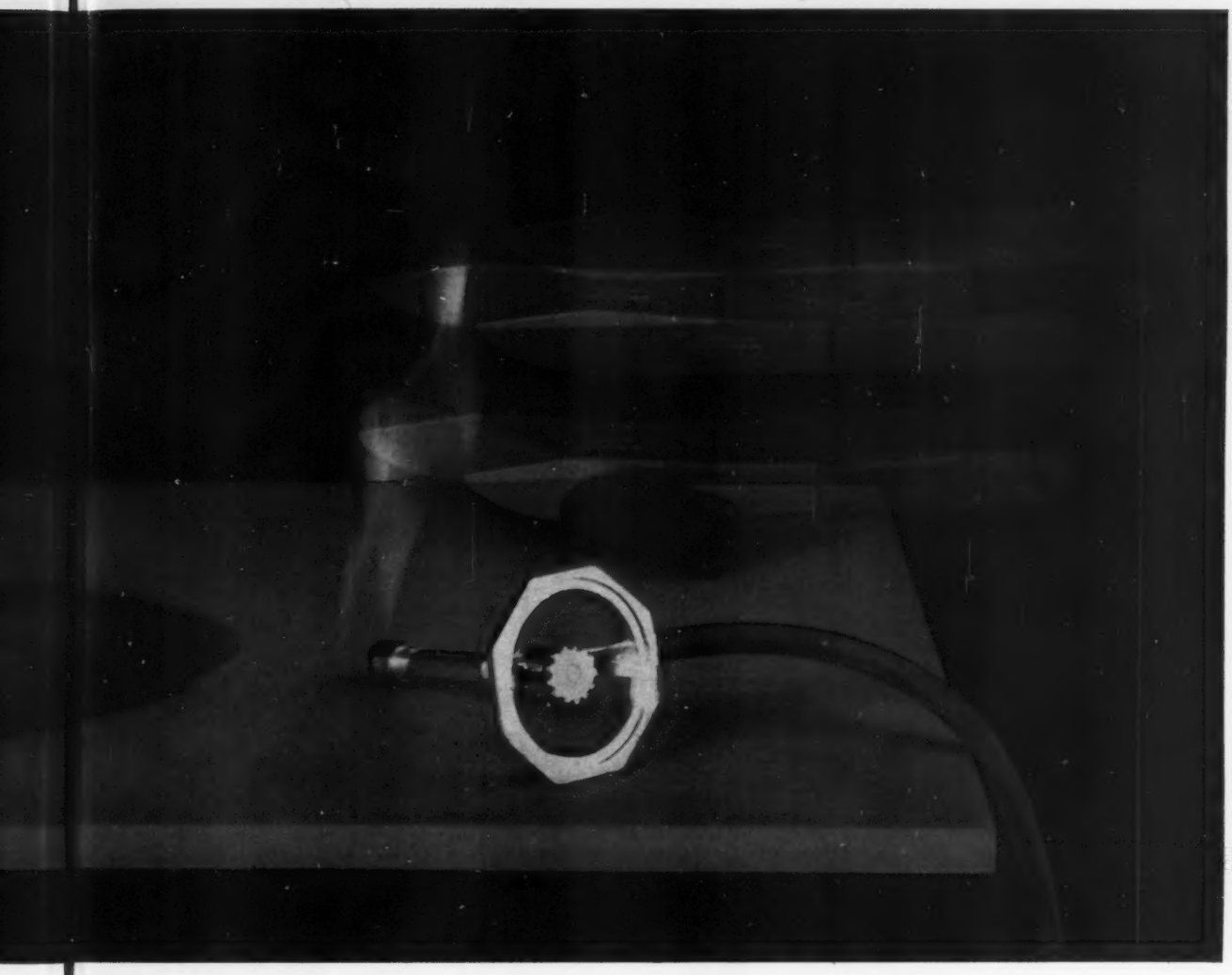

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through a Büchner funnel containing glass beads a size finer than those in the electrophoresis cell; these remove any sediment or dust in the solution and keep the cell bed clean. The filtered buffer is pumped into a polyethylene "head" bottle mounted on a sliding carriage on one of the columns that support the electrophoresis cell. An overflow tube in the bottle determines the height of the liquid column and hence the pressure in the system. By moving the bottle up or down, the operator can control the rate of buffer flow.

The buffer is cooled before it enters the top of the cell by passage through a small condenser. It then enters the top of the electrophoresis chamber through a forked tube—one side carrying the full flow, the other comprising a capillary which maintains a trickle of buffer to keep the bed of beads moist when the apparatus is not in use.

The sample is injected into the top of the electrophoresis cell by means of a motor-driven syringe unit. As much as several tenths of a gram of sample can be introduced per hour; the volumetric feed rate is 10–30 ml/hour. The power supply provides a maximum of 1000 v, which corresponds to a potential gradient across the cell of 33 v/cm.

Continuous Flow Chromatograph

In the continuous flow electrochromatographs just described, the feature of continuous operation has been made possible by employing the electrical force at right angles to the forces of gravity and capillarity. It should be evident that this transverse force need not be electrical in nature; any means of creating two velocity vectors at an angle to each other (see Figure 38F) should be similarly applicable. Indeed, a continuous flow chromatograph has recently been described, and is commercially available, in which the transverse vector is a mechanical motion imparted to the specimen by means of a turntable mechanism. The

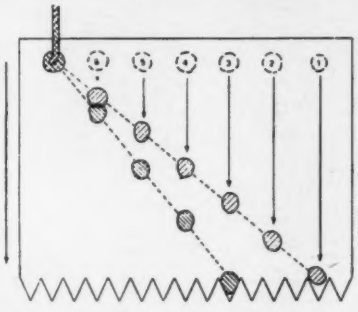

Figure 44. If a specimen consisting of two components is placed on the paper at equidistant points in a definite time sequence, while chromatographic development is continually occurring, the individual components will follow different paths along the paper.

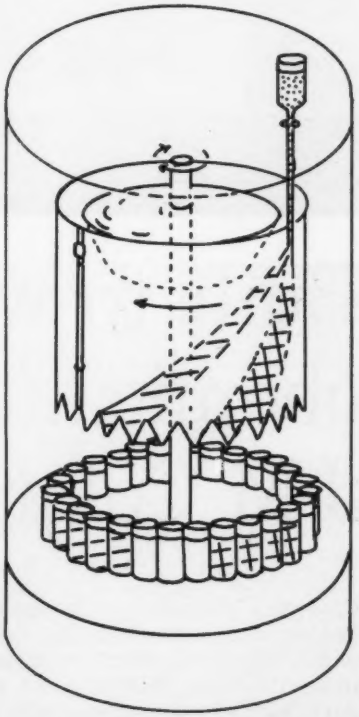

Figure 45. If the ends of the paper sheet of Figure 44 are joined to form a cylinder, and the cylinder is rotated, it is possible to choose the rate of rotation so that a given component will always drip off the sheet above a certain receiver. This is the principle of the design of the Collectochrom.

(*Continued on page A732*)

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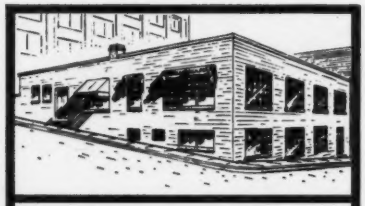
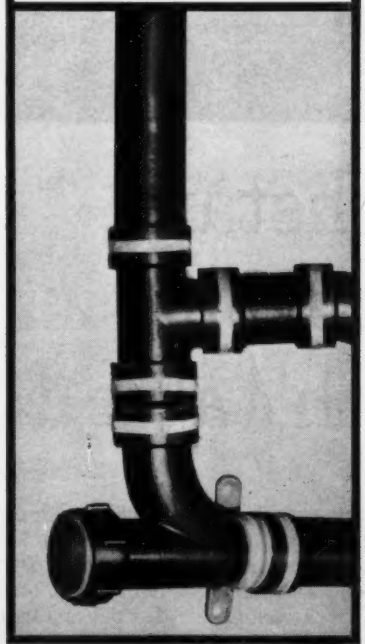


Waste and vent systems for 8 large photoengraving etching machines are piped with Vulcathene in this Virginia Engraving Co. plant in Richmond, Va. Contractor was B. & G. Olsen, Richmond, Va.



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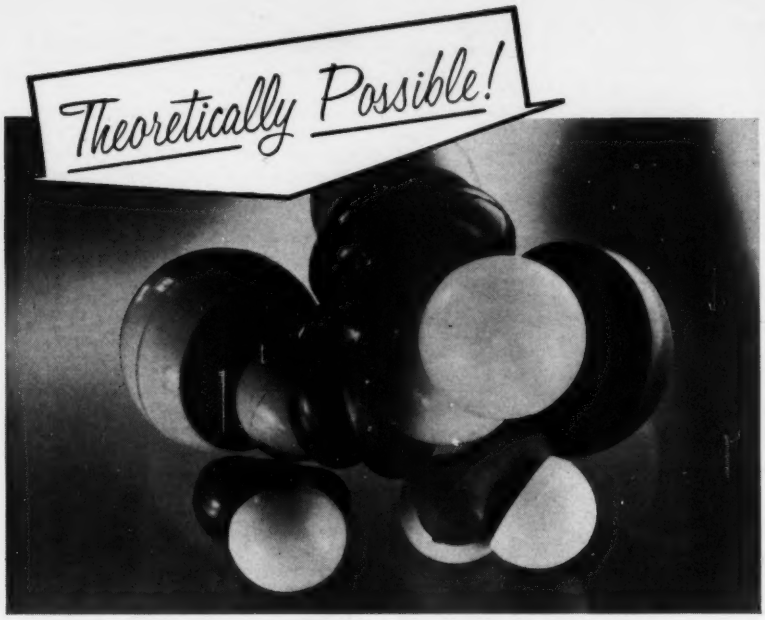

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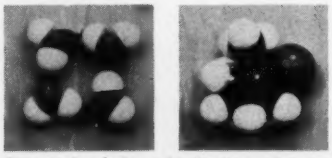

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principle of this approach may be made clear by reference to Figure 44.

Suppose that equal amounts of a specimen, containing only two components, are positioned at seven equally spaced locations along the top of a filter paper sheet *in successive time sequence*, i.e., first, spot *1* is added, then after a certain interval of time, spot *2*, then spot *3*, etc. A continuous flow of background electrolyte (buffer) takes place during the application of these sample spots. Then, by the time spot *7* is being applied, the components of sample *1* have been chromatographed a considerable distance down the sheet, sample *2* has moved down somewhat less, sample *3* still less, etc., as shown in Figure 44. It will be noted that at the instant of time shown in the diagram, the slower moving component is ready to drip off the drip tip below position *1*, and the faster moving component is ready to drip off below position *3*. Some time later, a slow component will drip off below position *2* while a fast component is dripping off below *4*. As time advances, this *separation in distance* between the points at which these two components drip off remains constant, although the pair of drip tips involved moves toward the left in the diagram. If, therefore, the paper sheet is rolled into a cylinder, and the cylinder is rotated toward the right at the proper rate, a set of non-moving receivers can be placed below the drip tips and a given component migrating down the paper will always reach a drip tip just when that tip is over a given receiver. This design of the experiment is illustrated in Figure 45, which shows a sample reservoir feeding continuously onto a rotating cylindrical sheet. Solvent constantly washes down the sheet and moves the components of the sample down until they finally drip off into the stationary receivers.

An instrument of this design is manufactured by Pleuger and Co., Belgium and is available in the U. S. through, LaPine Scientific Co., Chicago 29, Illinois (Collectochrom, $975).

Fraction Collectors

When an electric potential or a directed motion of the specimen is applied transverse to the direction of flow of the bulk liquid phase, the sample components are spread out in *space*, and continuous, *simultaneous* collection of all components is practical, as in the devices just described. However, there are many situations, as e.g., in column elution chromatography, where the sample components are spread out in *time*, and techniques are required for collecting the components in *sequence*.

The simplest types of fraction collectors do not attempt to *sense* the composition of the effluent and make decisions as to when to switch from one receiver to another on the basis of the chromatographic pattern. Rather, these devices simply automate the collection of fractions of the liquid issuing from the column according to a purely arbitrary plan. The principal methods of fraction cutting

(*Continued on page A734*)

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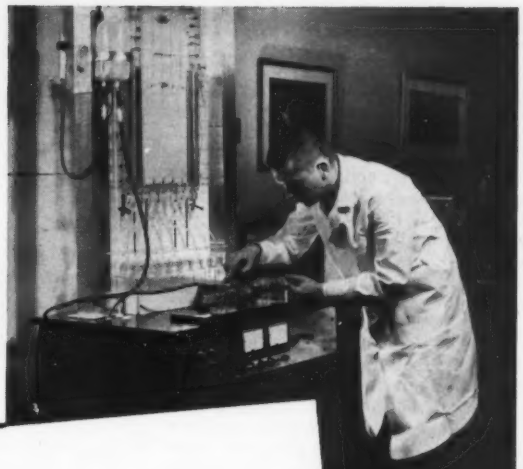

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commercially available are: (*1*) equal times of flow, (*2*) equal volumes collected, and (*3*) equal numbers of drops counted.

A time-flow fraction collector consists of a timer, a relay, and a tube indexing or advancing mechanism. When a given time interval has elapsed, the relay is activated, and the effluent from the column is diverted from the tube it was filling to a new tube. An example of this type of device is the Calbiochem Fraction Collector (No. 85000, $585) available from California Corporation for Biochemical Research, Los Angeles 63, California, and shown in Figure 46. The time interval is adjustable from 4 to 240 minutes. The column effluent is led through a plastic tube and allowed to issue at a point above one of the collecting tubes. The plastic tube is clamped in a movable head which travels along a horizontal track, and repositions the effluent over a new collecting tube after each signal received from the timer unit.

In other designs of time-flow fraction collectors, the location of the effluent tube remains fixed, and a turntable positions a new tube under it in response to the impulse from the time control unit.

If a time-flow fraction collector is to yield equal volumes of effluent during the course of a chromatographic elution, the rate of flow of liquid from the column must be held constant. This requires that the hydrostatic head of liquid in the column, as well as the tightness of the column packing, degree of swelling, viscosity, surface tension, etc., be constant throughout the run. Since it is often difficult to achieve this manner of control, some effort has been devoted to the elaboration of fraction collectors that are not subject to these aberrations.

(*Continued on page A736*)

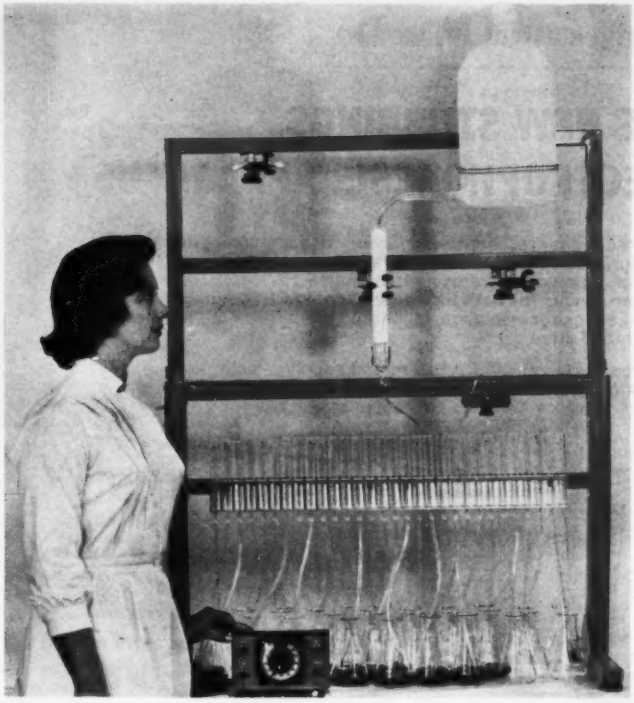
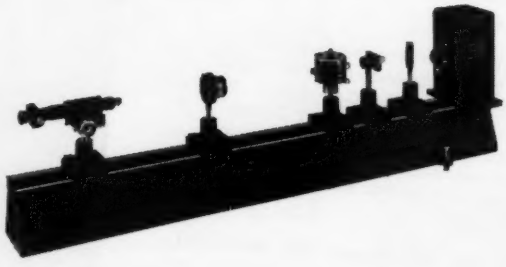


Figure 46. The time-flow fraction collector of California Corporation for Biochemical Research.

Direct Measurement of Difference in Refractive Index



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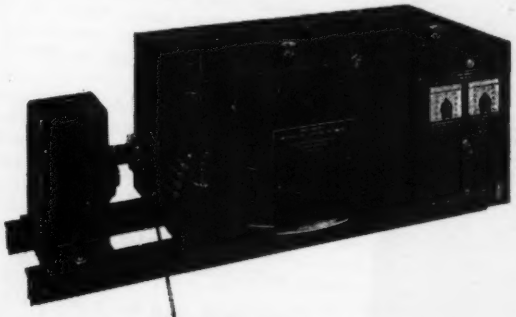

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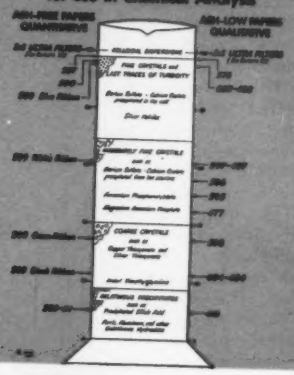

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The principle of operation of a volumetric fraction collector is illustrated by the diagram in Figure 47, which shows the Buchler Instruments, Inc., volumetric siphon (Siphon plus Activator-Relay unit, about $100; turntable with index mechanism and space for 120 test tubes, $295). When the amount of liquid that has been collected is small, there is an open circuit in the trigger unit, as shown in the diagram on the left in Figure 47. When enough liquid has been collected to bring the level in the outflow arm (extreme right) to the top bend, a spontaneous siphoning will take place, and the container will empty itself. Just before this happens, the hydrostatic pressure of the liquid in the siphon has built up enough to cause the electrolyte in the trigger unit to rise in the index tube enough to make contact between the electrodes. This sends an impulse to the turntable, which is caused to advance one position, and puts an empty test tube in position to receive the liquid when it siphons out.

An example of the construction of a drop-counting unit is shown in Figure 48. As each drop falls, it intercepts and disperses a light beam which otherwise illuminates a photocell. The resulting diminution in intensity at the photosensitive surface creates an electrical impulse which is fed into a counter-register unit. The register can be arranged to trigger the indexing of a turntable after any given number of drops has been counted. A detector of this type with a totalizer-selector that can be set for up to 800 drops per fraction is made by National Instrument Laboratories, Inc., Washington, D. C. (NIL-Riggle Photoelectric Drop-counter, $550).

(*Continued on page A738*)

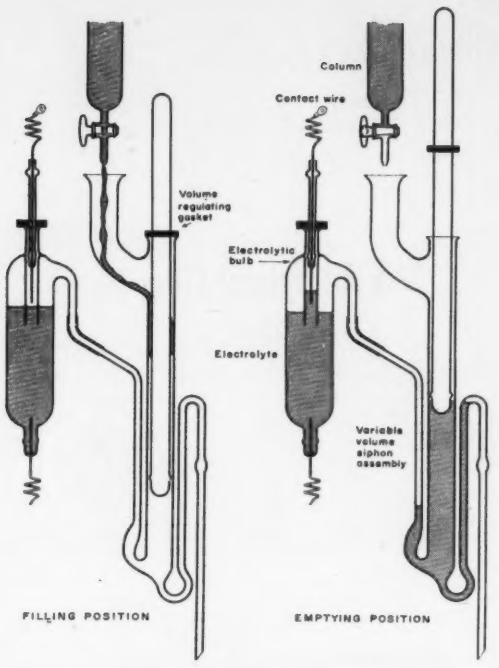

Figure 47. The principle of operation of the volumetric siphon type fraction collector. As the siphon assembly fills with liquid, the increase in pressure causes contact to be made in the electrolytic bulb. This sends an impulse to the relay unit and advances the turntable one position. When the liquid level in the siphon reaches the top of the bend in the overflow arm, the entire contents siphon out.

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Fraction collectors of all three types described above (either individually, or collectively) are available from a number of sources:

Chromatography Corporation of America, Chicago 26, Illinois: (*No. 1000, a 240-hole turntable wired for time-flow, volumetric siphon, and drop counting, $850*).

LKB Instruments, Inc., Washington 14, D. C.: (*RadiRac Automatic Fraction Collector; a variety of assemblies available ranging from a circular 60-tube turntable wired for time and volume only, $467, to elaborate units of 240-tube, circular, spiral, and square-wave type turntables wired for time, volume and drop-count, about $1500*).

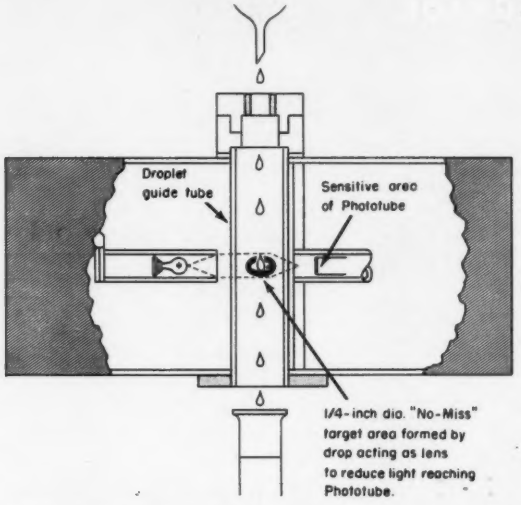
Droplet guide tube
Sensitive area of Phototube
1/4-inch dia. "No-Miss" target area formed by drop acting as lens to reduce light reaching Phototube.

Figure 48. The sensing unit of a drop counter. Each drop intercepts the light beam and causes a diminution of the intensity received by the photocell.

Shandon Scientific Company Ltd., U. S. Distributor Consolidated Laboratories, Inc., Chicago Heights, Illinois: (*an automatic fraction collector which collects fractions by weight*).

Research Specialties Co., Richmond, California: (*fraction collectors available in each of the three basic types; an assembly comprising all is about $1000*).

Rinco, distributed through laboratory supply houses: (*turntable with time and volume collection, $530; photoelectric drop-counter, $580*).

Bender and Hobein, distributed in U.S. by Harshaw Scientific Co., Cleveland 6, Ohio.

Packard Instrument Co., Inc., LaGrange, Illinois: (*fraction collectors especially designed for use with radioactively labelled specimens*).

Vanguard Instrument Co., LaGrange, Illinois: (*a complete line of automatic fraction collectors and accessories*).

Gilson Medical Electronics, Middleton, Wisconsin: (*all types of fraction collectors*).

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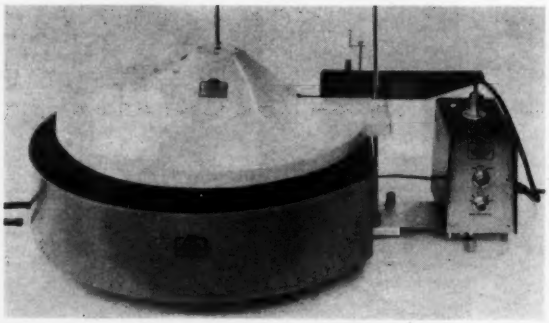

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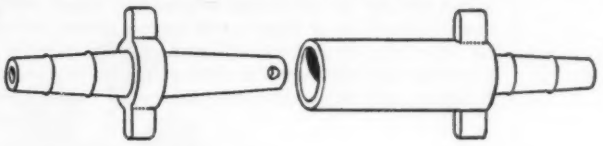

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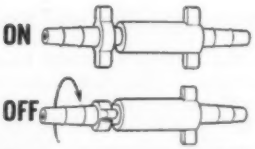

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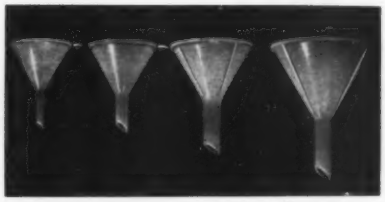

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● Technical Bulletin No. 511, *Metal Hydrides for Hydrogen Generation*, describes how metallic hydrides can be used for "in-situ" generation of hydrogen through their interaction with water. The bulletin is available from Metal Hydrides Inc., 12-24 Congress St., Beverly, Massachusetts.

● Copies of *Catalystings*, a quarterly publication by Wilkens-Anderson Co., 4525 W. Division St., Chicago 51, Illinois, are now available free upon request. Manufacturers and distributors of laboratory equipment and supplies, Wilkens-Anderson issues *Catalystings* to review new and improved products in their extensive line.

● *Platinum Metals Review* Volume 5, Number 3, July 1961 is now available from the J. Bishop and Co., Platinum Works Malvern, Pennsylvania.

● Hazelton-Nuclear Science Corp., 4062 Fabian Way, Palo Alto, California, announces their new catalogue which describes a line of radio-active services and ultra-pure labeled compounds.

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(*Continued on page A743*)

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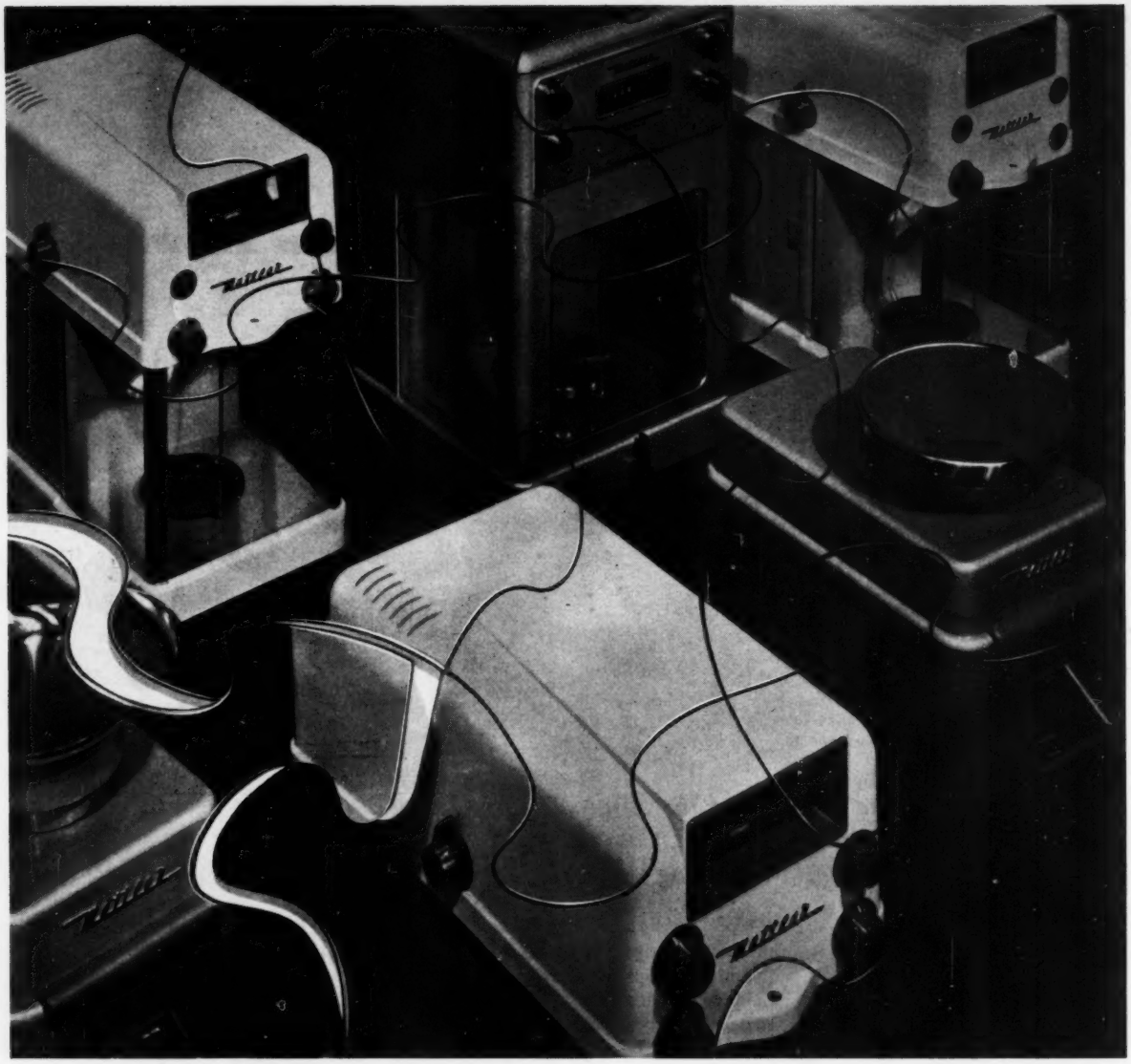

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Out of the EDITOR'S BASKET

● Minneapolis-Honeywell Regulator Co., Station M389, Wayne and Windrim Ave., Philadelphia 44, Pennsylvania, announces the second revision of *Catalogue G-10b, Scientific and Test Instruments.*

● Pfanstiehl Laboratories, 1219 Glen Rock Ave., Waukegan, Illinois, have published a new and enlarged 46-page catalogue of biochemicals, including rare sugars, amino acids and derivatives. A new feature of the 1961 catalogue is the inclusion of structural formulas in addition to specifications, systematic names, plus commonly used synonyms and prices.

● *Patent Intelligence File Co.*, 187 Olive St., New Haven, 11, Connecticut, now supplies Patent Digests as published in the Official Gazette. A brochure with details on this service is available on request.

● Sargent *Bulletin ST* describes in detail the Sargent spectrophotometric and potentiometric titrators and their applications. These instruments are equipped for those titrations which provide potentiometric end points from the four general classes of acid base, oxidation reduction, precipitation, and complex formation. Write for your copy: E. H. Sargent & Co., 4647 W. Foster Ave., Chicago 30, Illinois, Dept. ST.

● A revised and greatly expanded data bulletin on n-butyl alcohol has just been released by U. S. Industrial Chemicals Co. It is specifically designed to provide information on n-butyl alcohol for the surface coatings and chemical processing industries. Copies are available from Technical Literature Department, U. S. Industrial Chemicals Co., 99 Park Ave., New York 17, N. Y.

● The storage, transfer and measurement of methyl chloride are covered in a new bulletin just issued by Ansul Chemical Co., Marinette, Wisconsin. The company points out that the bulletin applies equally well to other liquefied gases.

● A "New Product" section containing 179 new products high-lights the *Reference Guide and Price List No. 021 for Research Biochemicals* just issued by Mann Research Laboratories, 136 Liberty St., New York 6, N. Y.

● Publication of a new catalogue on high vacuum technology and products has been announced by the Vacuum Products Div., Varian Associates, 611 Hansen Way, Palo Alto, California.

● A new, 240 page multi-color catalogue *No. 161*, illustrating and describing Blue M Electric Company's complete line of electric ovens, furnaces, baths, environmental cabinets, related temperature control equipment and accessories for laboratory, pilot plant, and production is available on request from Blue M Electric Co. 138th and Chatham St., Blue Island, Illinois.

(*Continued on page A744*)

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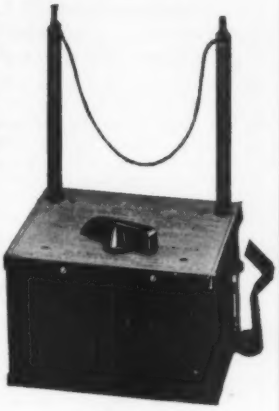

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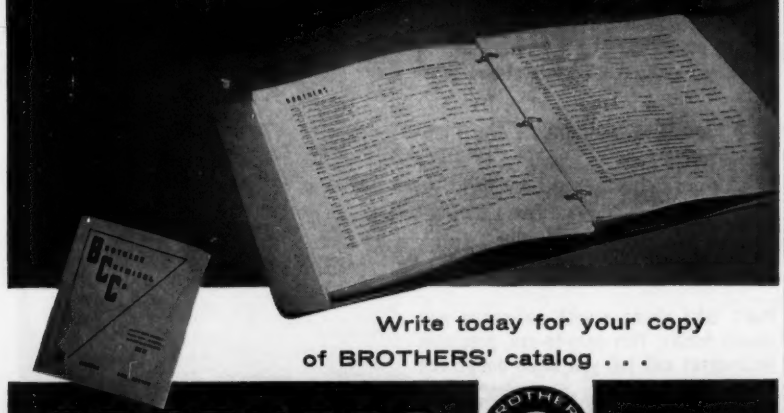

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● Order the following from O.T.S., U. S. Department of Commerce, Washington 25, D. C., by number:

PB 171 596: *A Study of the Nature of Free Radicals in Irradiated Chemical Systems.* P. Y. Feng and others, Armour Research Foundation of Illinois Institute of Technology, for Wright Air Development Division, U. S. Air Force. November 1960. 65 pages—$1.75.

PB 171 563: *Stereospecificity and Dielectric Properties of Polar Polymers.* H. H. Zabusky and H. A. Pohl, Plastics Laboratory, for Office of Naval Research, Department of the Navy. August 1960, 52 pages—$1.50.

IS—178: *Low - Cost Bridgman - Type Single-Crystal Growing Apparatus.* E. H. Olson, Ames Laboratory, Iowa State University of Science and Technology, for U. S. Atomic Energy Commission. August 1960, 51 pages—$1.25.

PB 171 530: *Properties of Solutions in the Neighborhood of the Critical Temperature of the Solvent.* S. W. Benson and others, University of Southern California, for U. S. Government. April 1961, 25 pages, 75 cents.

Miscellany

★ Why U. S. physicist and chemists do not read more than an estimated five percent of the current professional literature published in their fields is explored in a National Science Foundation-sponsored study released to science and industry through the Office of Technical Services.

A total of 701 scientists took part in the survey–297 chemists and 404 physicists. "Data concerning the scientist's reading behavior were obtained by self observation by the scientist over a consecutive 14-day period." Then, the test subjects were furnished questionnaries and wired for sound. Actually, each was given a "Random Alarm Mechanism." The RAM is "an electronic device about the size of a package of cigarettes which was designed to emit audible alarms at random moments."

When the alarm sounded, if the scientist was reading a scientific periodical he filled out a short questionnaire indicating the nature of his reading matter. "If he was not reading a scientific periodical when the alarm sounded," he merely put a check mark on the questionnaire. The possibility of the self-conscious scientist, purposely or subconsciously, altering his reading habits during the survey period was taken into consideration. Each scientist's identity was protected, and he was requested "not to consciously alter (his) normal pattern of journal reading."

Other parts of the study included "significant variables which are under the publisher's control" and a "cost equation."

The study *PB 171 503* may be obtained from the O.T.S., U. S. Department of Commerce, Washington 25, D. C., for $2.00.

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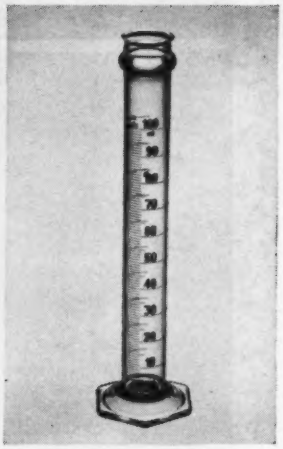

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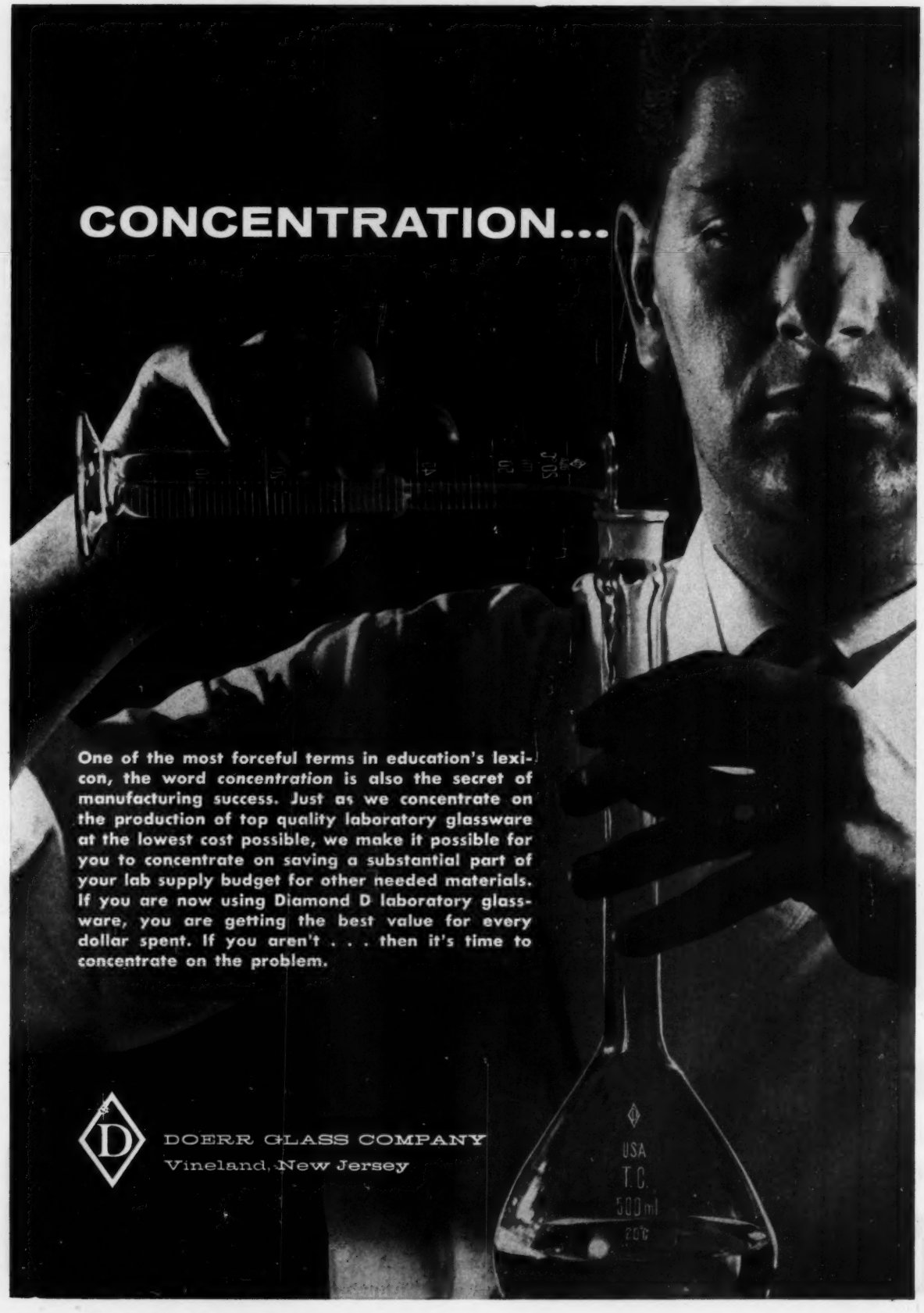
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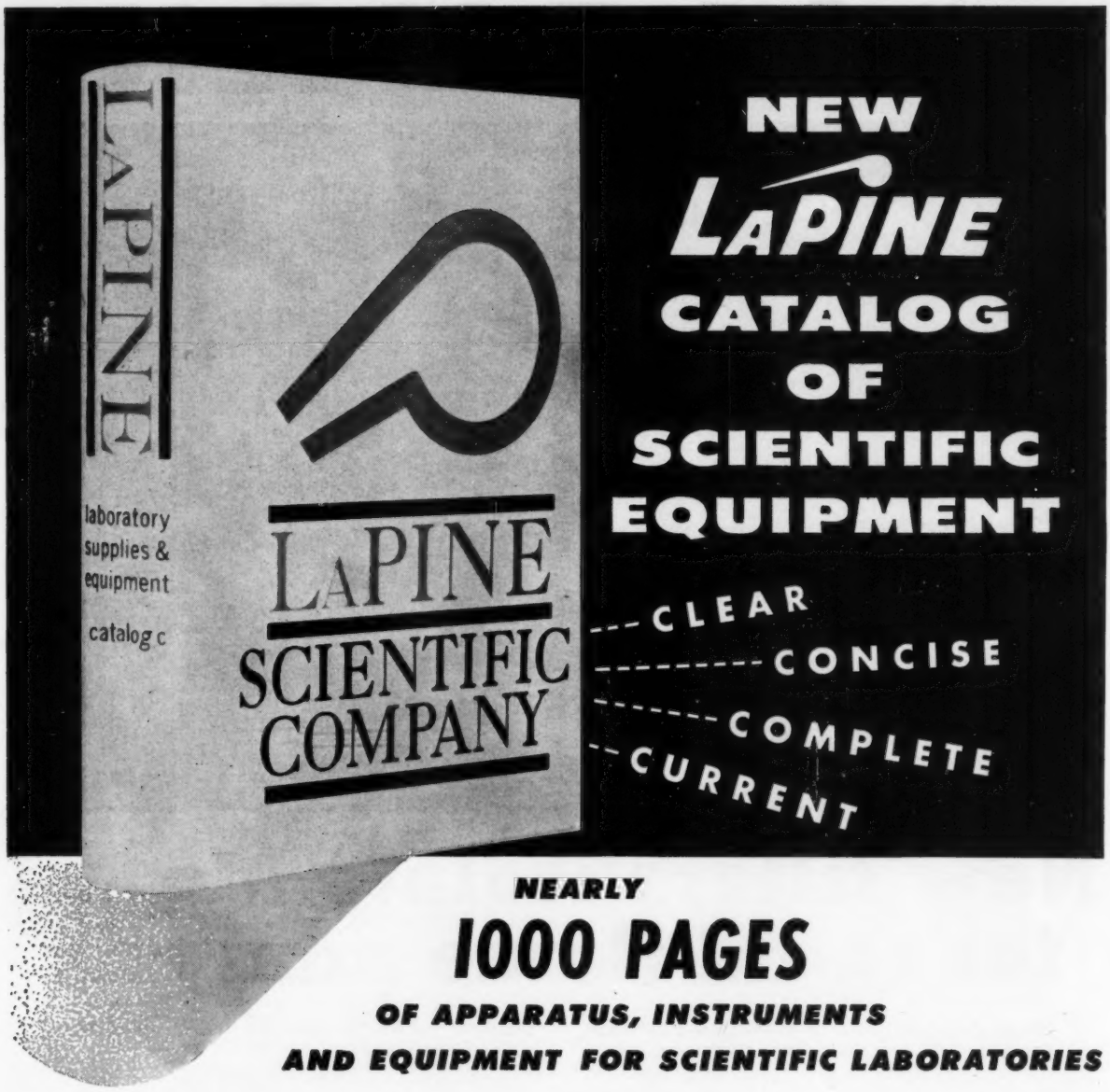

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DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

"VISIBLE" MONOMOLECULAR FILMS

A Chem Ed TESTED DEMONSTRATION

Estimation of Molecular Size and Avogadro's Number

Submitted by: L. Carroll King, Northwestern University, Evanston, Illinois
Checked by: James R. Mills, Southfield High School, Southfield, Michigan

PREPARATION

Set up a series of four test tubes each containing 9.0 ml of pentane. Add 1.0 ml of oleic acid to the first, transfer 1.0 ml of this solution to tube 2, and so on. Tube 4 will contain 0.001 ml of oleic acid per 10.0 ml of solution.

A plastic cake dish, 15 × 20 × 9 cm, is filled with water until the water surface is above the edge of the dish; add one drop of concentrated hydrochloric acid to the water. Clean the water surface with a lucite barrier, 17 × 2 × 1 cm, cover with "piston oil," and dust with lycopodium powder.

DEMONSTRATION

Place 0.10 ml of the solution in tube 4 (1×10^{-5} cm^3 of oleic acid) on the surface of the measuring tray. After evaporation of the pentane, the oleic acid film is easily visible since it will push back the piston oil and lycopodium powder and form an approximately circular area on the water surface.

REMARKS

The area of the film may be measured by outlining the film on a glass plate, transferring the outline to a piece of graph paper graduated in millimeters, and counting the squares. From the known volume of oleic acid in the film and from its area, the thickness of the monomolecular film can be calculated. Calculation of Avogadro's number from this data was discussed by King, L. C., and Neilsen, E. K., J. Chem. Educ., **35,** 198 (1958). "Piston oil" may be prepared by heating "Hyvac" oil for eight hours at 300°C or until it forms a film. [See also Kuehner, A. L., J. Chem. Educ., **19,** 27 (1942)].

DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

FIRE UNDER WATER

A Chem Ed TESTED DEMONSTRATION

Submitted by: R. B. Escue, North Texas State University, Denton, Texas.
Checked by: Berta May Pope, Arlington High School, Arlington, Texas.

PREPARATION

Fill a conical vessel or a 100-ml graduated cylinder (size 3) almost full of water. Add sufficient potassium chlorate without stirring to form a layer of the solid about 5 mm thick at the bottom of the vessel. Cut a piece of white phosphorus the size of half a pea into 4 or 5 smaller pieces. Drop into the graduate so that the phosphorus remains on top of the $KClO_3$ layer.

DEMONSTRATION

Place a long thistle tube so that its outlet is near the phosphorus pieces and slowly pour separate small (0.5 ml) portions of concentrated sulfuric acid into it. Allow the reaction to diminish after each addition. Soon bubbles of gas will form that will cause sparks as they contact the phosphorus. The "fire" or sparks readily seen in a darkened room are produced under water.

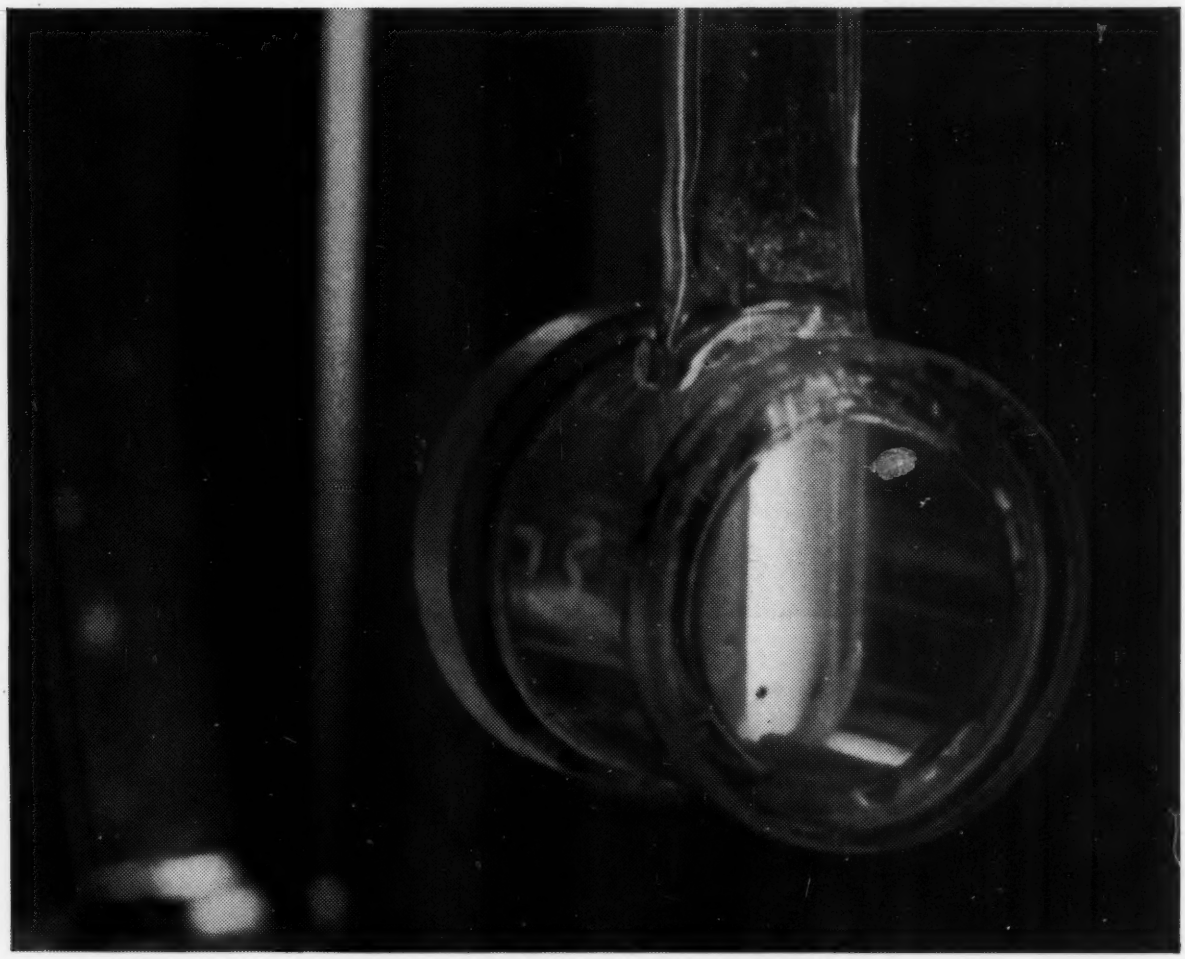
REMARKS

The gas probably is a mixture of chlorine dioxide and oxygen.

$$4KClO_3 + 2H_2SO_4 \rightarrow 2K_2SO_4 + 4\ ClO_2 + O_2 + 2H_2O$$

Do not add any fresh potassium chlorate to the acidified mixture. When the demonstration is concluded, decant most of the fluid without exposing the phosphorus to air. Add fresh water to dissolve the potassium chlorate residue. Continue decanting and washing until only phosphorus remains for disposal by burning.

from abstract ideas...fundamental knowledge at Esso Research



New insight into the interaction between hydrocarbons and catalytic surfaces has been acquired by Esso Research scientists using advanced techniques for fundamental studies of adsorption on heterogeneous catalysts. The first results were obtained from a detailed infrared study of adsorbed acetylenes.

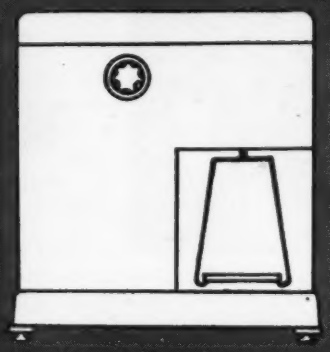
Acetylene, deuteroacetylene, methyl and dimethyl acetylenes are strongly chemisorbed on alumina even at room temperature. The first three can also exist in a weakly adsorbed state. The strongly held species are held perpendicular to the surface through the acetylenic hydrogens, except dimethyl acetylene, which is held parallel to the surface. All the weakly held acetylenes are held parallel to the surface. The sites responsible for the strong chemisorption of acetylenes are different from those responsible for the strong adsorption of dimethyl acetylene. Surprisingly, no strong chemisorption of either acetylene or dimethyl acetylene was observed with silica.

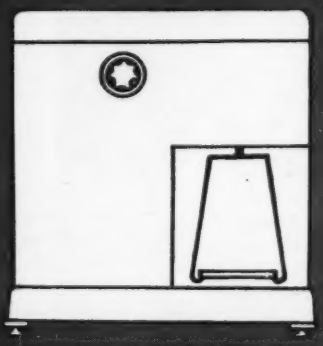
These results raise several challenging fundamental concepts. Thus, the head-on adsorption is quite unexpected for a molecule containing a reactive triple bond, and it is perhaps surprising that only substitution by two inductive methyl groups can activate the acetylenic triple bond sufficiently for sideways adsorption. Finally, the great difference between SiO_2 and Al_2O_3 raises important questions concerning the role of the oxide in the adsorption.

This work is continuing together with other basic studies of adsorption on catalysts including such advanced methods as microcalorimetry and conductivity.

...adapted from a scientist's notes at Esso Research and Engineering Company P. O. Box 45B, Linden, New Jersey.

OUTWARD APPEARANCES ARE *Deceiving*





These two balances with the same outward appearance are fundamentally different. Both are single-pan, but one is a 2-knife-edge substitution balance, the other a 3-knife-edge, equal-arm balance.

This difference is of the greatest significance to instructors who use the balance to teach the principles of weighing or of measurement in general.

Teaching with a 3-knife-edge, single-pan balance, the instructor will explain that one major systematic error can be caused by inequality of the supposedly equal beam arms. As a corollary, he will show the students how the error can be checked quantitatively. Unfortunately, the construction of most 3-knife-edge, single-pan balances is such that this check is quite difficult to make for anyone but a trained balance technician. And transposition weighings, to eliminate the error, are not possible on these balances.

A system of measurement with a systematic error but no simple way to check the extent of the error is hardly one to use for teaching purposes

The 2-knife-edge, single-pan substitution balance compares object and weights on one and the same beam arm. It measures them with the same yardstick. A lever arm error cannot exist. This type of balance demonstrates to the student quite vividly how proper selection of the measuring method can reduce the number of systematic errors

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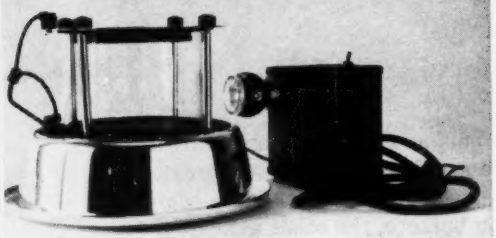

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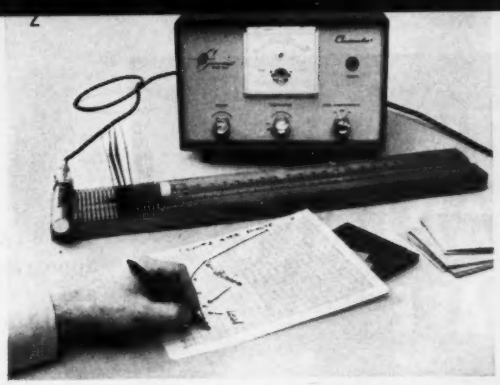

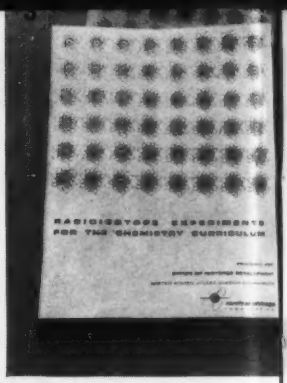

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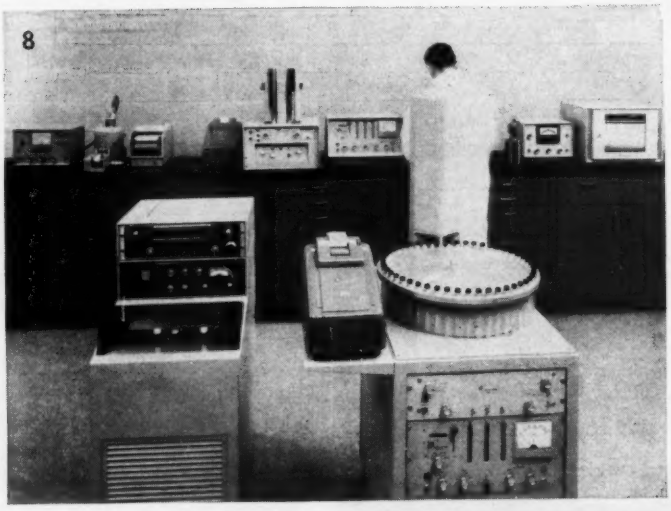

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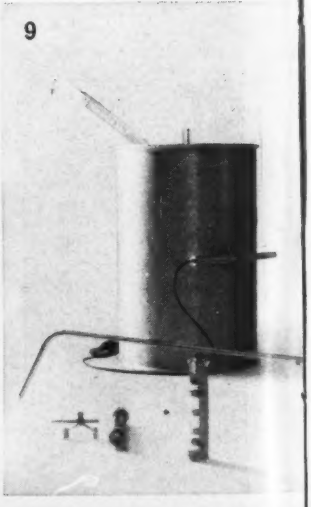

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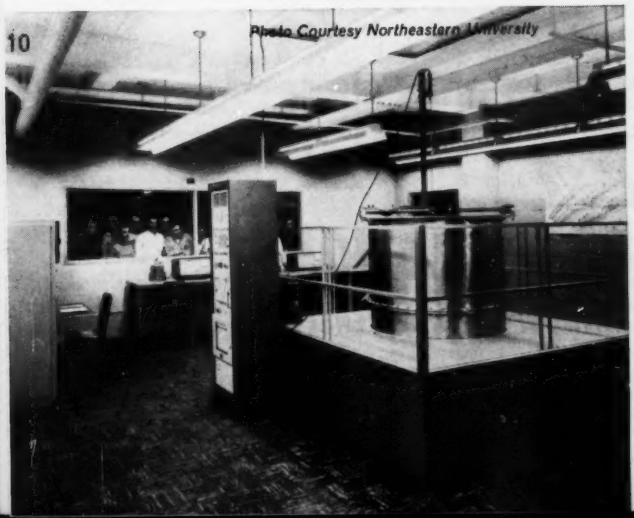

Photo Courtesy Northeastern University

11

Photo Courtesy Shell Oil Company

How to bring radioisotopes into your chemistry curriculum

Read how these Nuclear-Chicago products help to enlarge the scope of chemical education and also serve graduate and faculty research needs

RADIOISOTOPE procedures offer chemistry students penetrating insights into the laws of nature. Forward-looking educators are using the equipment illustrated at the left in lectures, for student experiments, and in research. These eleven photographs suggest the scope and completeness of Nuclear-Chicago's instrument line for teaching and research. Systems range from low-cost equipment for demonstration to sophisticated instrumentation for fundamental investigation. All are characterized by reliability, precision, versatility, and inherent safety.

Chemistry departments now employing radioisotope techniques will want to consider program expansion to take advantage of the newer products illustrated. Others may well regard the apparatus presented here as a planning guide.

Low-cost demonstration equipment for the nuclear age became a reality with the introduction of Nuclear-Chicago's Cloudmaster® and Classmaster®. The Cloudmaster (figure 1) is a continuously sensitive cloud chamber that provides a spectacular display of ionization tracks caused by alpha, beta, gamma, and meson radiation. The Classmaster (figure 2) is a complete system for demonstrating radiation absorption, scattering, geometry effects, coincidence loss, etc. In addition, it permits simple tracer experiments using license-exempt radioisotopes. Both instruments enjoy wide acceptance because of their simplicity of operation and the vivid, easily-understood presentations they make possible.

Thirty-three student experiments that fit naturally into the chemistry curriculum without requiring changes in basic course content are contained in a new 187-page experiment manual and 60-page companion volume of instructor notes (figure 3) developed by Nuclear-Chicago under contract with the Atomic Energy Commission. Model 4001 nuclear training system (figure 4) is offered with isotopes, sample preparation equipment, and instruments to perform all the experiments covered in the manual. The system features ease of sample preparation using the chimney funnel shown in figure 5.

Model 4001 is supplied with the long-lived radionuclide set RNS-110 (figure 6) and the radionuclide certificate book RCB-1 (figure 7) with which the instructor can order short- or long-lived isotopes as they are needed. Neither requires an AEC license to purchase or use, and both are available individually.

As student mastery of radioisotope procedures advances, a chemistry department will next want to consider establishing a complete nuclear laboratory for precision handling, detection, and counting of beta- and gamma-emitting isotopes. Such a facility has valuable application to qualitative and quantitative studies at both the graduate and undergraduate levels. A typical installation is pictured in figure 8. In the left foreground is the Model 701 liquid scintillation detector with Logic scaler, and at the right is the Model C120 automatic sample changer for gamma-emitting liquids or solids in test tubes. In the background, from the left, are the Actigraph II® system for scanning radiochromatograms, a low-background automatic sample changer for solid beta samples, and the Dynacon® electrometer for high-efficiency measurement of beta samples in the gaseous phase.

At this stage, the ideally equipped university will lack only the means to create its own radioactive isotopes and to study reactor techniques and fundamental nuclear properties. For these basic needs, Nuclear-Chicago offers a three-step program.

First, undergraduate departments will choose the NH3 neutron howitzer (figure 9) for experiments with low-level neutron sources, production of short-lived, low-intensity radioisotopic tracers, and low-flux activation analysis.

Second, the chemistry, physics, and engineering faculties will often cooperate in establishing an advanced training facility centered on the inherently safe Model 9000 subcritical assembly (figure 10). Characteristics of this water-moderated, natural uranium assembly are nearly identical in nature to those of a full-scale power or research reactor, and the student readily masters the fundamentals of reactor theory and design.

Finally, the long-felt need of university research scientists for a versatile, relatively inexpensive, high-intensity neutron source can be well satisfied by the TNC neutron generator designed and manufactured by Nuclear-Chicago's subsidiary, Texas Nuclear Corporation (figure 11). Providing a controllable yield of 4×10^{10} neutrons per second and a thermal neutron flux of greater than 10^8 using an appropriate moderator, the generator is widely employed in activation analysis, process control, applied research and development, and fundamental investigation.

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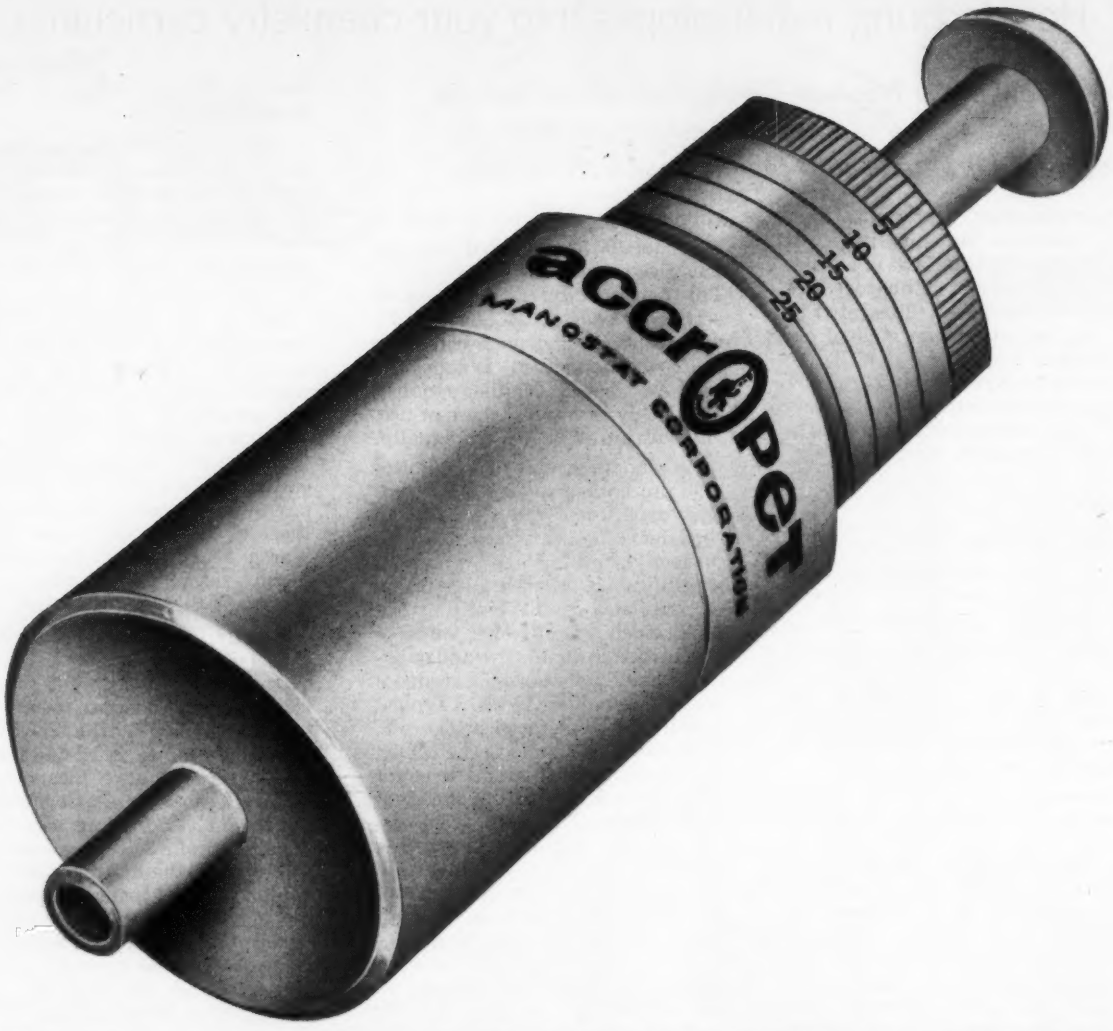

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JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

The Iodometric Titration of Arsenite in Alkaline Solutions

See McAlpine, R. K., *J. Chem. Educ.*, **26**, 362–6 (1949).

Iodine solutions are usually standardized against a reducing agent which is itself a primary standard. Of these, As_2O_3 is probably most commonly used, based on the classical work of Washburn in 1908. However, as McAlpine points out, there is some reason to question the validity of the conclusions drawn by Washburn from his data. In particular, when the iodine reagent is added to an alkaline solution of arsenite, two reactions can take place, the desired reaction which is the oxidation of arsenite to arsenate, and the formation of IO_3^- and I^- which will lead to an erroneous result. In alkaline solutions, up to a *p*H of 10, this second reaction takes place to a negligible extent, but at higher *p*H's the error becomes serious, though it can be minimized by adequate swirling, at least up to a *p*H of 11.

These conclusions are based upon a consideration of the reactions that can occur under various conditions, together with a detailed discussion of the equilibria that are involved. McAlpine's treatment is detailed, though quite clear and understandable to the careful reader.

Questions:

Show that iodine can be standardized against arsenic trioxide if the *p*H of the reaction mixture is properly controlled.

Is it true that IO^- will disproportionate and that this disproportionation will lead to erroneous results in strongly alkaline solutions?

In some cases, as described by McAlpine, the blue color (with starch indicator) which appears at the end point slowly fades away. Account for this decolorization and verify your explanation by further experimental work.

Under what conditions can iodine be oxidized by the oxygen in the air to IO_3^-?

Is it true that at higher concentrations of I^-, the error due to the formation of IO_3^- is reduced?

McAlpine describes a simple, effective procedure which demonstrates that NH_4^+ is an acid. What other evidence can you find, from the results of your laboratory work, which indicates that this ion is acidic?

Tris(hydroxymethyl)aminomethane as a Titrimetric Standard

See Whitehead, T. H., *J. Chem. Educ.*, **36**, 297 (1959).

Like other amines, tris(hydroxymethyl)aminomethane, $(CH_2OH)_3CNH_2$, is a base. It can be used as a titrimetric standard in place of sodium carbonate. It is commercially available in pure form.

Questions:

The ideal titrimetric standard possesses certain properties. Identify these and determine that tris(hydroxymethyl)aminomethane does or does not possess these properties to a sufficient degree to warrant its use as a titrimetric standard.

From your laboratory work, show that tris(hydroxymethyl)-aminomethane is or is not to be preferred to sodium carbonate as a titrimetric standard.

What other basic reagents might be suitable as titrimetric standards, in addition to sodium carbonate and tris(hydroxymethyl)aminomethane?

In addition to the indicators specifically mentioned by Professor Whitehead, can you suggest from your laboratory work any other suitable indicators when using tris(hydroxymethyl)-aminomethane to standardize an acid?

Titrations with Vanadium(II) Solutions for Elementary Quantitative Analysis

See Meites, L., *J. Chem. Educ.*, **27**, 458–9 (1950).

Solutions of vanadium(II) ion can be reproducibly oxidized to the trivalent state and, therefore, used in reductimetric titrations with ions such as iron(III) and chromium(VI). Details are given in the article. Primarily, precautions to prevent the air oxidation of vanadium(II) are all that are required. This is readily accomplished since vanadium(III) is readily reduced by amalgamated zinc in acidic solution. Meites describes the procedures necessary, and another method by which the vanadium solution to be reduced can be conveniently stored and dispensed directly into a buret is described by Martin, E. L., and Bentley, K. E., *J. Chem. Educ.*, **38**, 264–5 (1961).

In a titration with either iron(III) or chromium(VI), the end point is indicated by the use of thiocyanate ion. The color changes from red, due to the iron(III) thiocyanate complex, to green (or bluish-gray in the presence of chromium), the color of the vanadium(III) thiocyanate complex.

Questions:

Determine the concentration of iron(III) solutions by some other suitable method or by preparing such a solution from a known weight of iron that has been dissolved, as iron(III) ion, in a known volume of solution; compare this known concentration with that which you determine by a reductimetric titration with vanadium(II).

Similarly, compare the known concentration of a chromium (VI) solution with the value determined from a reductimetric titration using vanadium(II).

Can this reductimetric titration procedure be used to determine the concentration of other reducible ions, for example copper(II), titanium(IV), phosphorus(V), or manganese(VII)?

Meites states that in the beginning of a titration, some vanadium(II) is oxidized to an oxidation state higher than vanadium (III) but that these ions are later reduced to vanadium(III), so that, overall, only one electron is lost per vanadium(II) ion consumed in a titration. Can you confirm this statement?

In strongly acidic solutions vanadium(II) will reduce hydrogen ions to elemental hydrogen. Can this fact be put to any practical analytical use?

The Vitamin C Content of Fruits and Vegetables

See BURRELL, R. C., AND EBRIGHT, V. R., *J. Chem. Educ.*, **17**, 180–2 (1940).

The vitamin C content of several different vegetables and some fruits were determined. The results were found to vary widely, depending upon the variety, the stage of development when harvested, the time and conditions of storage, and other factors. Tillman's method for determining the ascorbic acid content was used. In this procedure, treatment with sulfuric and metaphosphoric acids formed a complex with the metal ions, inactivated ascorbic acid oxidase, and precipitated the proteins that were present. The aqueous solution was titrated with 2,6-dichlorophenol indophenol solution which was standardized against pure ascorbic acid. For an alternative iodimetric method see MOORE, C. E., *J. Chem. Educ.*, **25**, 671 (1948), AND GILKEY, W. A., *J. Chem. Educ.*, **24**, 458 and 468 (1947).

Questions:

Is it true that the vitamin C content of a vegetable or fruit is reduced by cooking the vegetable?

Under what conditions of storage can the loss of vitamin C during storage be minimized?

Show that the vitamin C content of a selected fruit or vegetable depends upon several factors, such as those mentioned above, or upon other factors such as climatic conditions during growth of the parent plant and maturation of the fruit or vegetable, the condition of the soil, the use of fertilizers, and other similar factors.

If time and available facilities permit, grow a vegetable or fruit (quickly grown vegetables, such as lettuce, onions, turnip greens, or dandelion greens are suggested) and determine which variables that affect the vitamin C content of the harvested vegetable can be easily controlled.

What other biochemically produced compounds can you isolate or identify in a selected fruit or vegetable? If quantitative analyses are possible, does the quantity of this compound show variations similar to those indicated for vitamin C?

The Chemistry of Flower Color Variation

See GEISSMAN, T. A., *J. Chem. Educ.*, **26**, 657–65 (1949).

In this article Geissman reviews the current views on the synthesis of the colored pigments present in flowers and shows that these suggestions are not inconsistent with information obtained from genetic studies of the same plants. The compounds responsible for the colors of some flowers are named in this article, but no experimental details describing their identification are given.

Question:

Select any flower you wish and, using Geissman's article as a starting point, identify the compound or compounds responsible for the color of the petals of the selected flower.

The Growing of Tomatoes and Cucumbers Without Soil

See KESSEL, W. G., *J. Chem. Educ.*, **22**, 360–1 (1945).

An introductory study of hydroponics is well suited for students who wish to undertake an interesting project which could eventually lead to a mature, sophisticated study of biochemistry. The beginner's requirements are simple: a water filled crock, a seedling, a few reagents, some simple accessory apparatus, and patience. This article discusses some of the important points that would be involved in a serious study of hydroponic phenomena, but it will be necessary to consult other references as well. The "Encyclopaedia Britannica" has more than one article on this subject, and also cites several excellent additional references.

Questions:

Determine the optimum composition of the aqueous media used in the hydroponic culture of any plant you select. Does this optimum composition vary as the temperature, humidity, or other conditions are varied?

What are the essential inorganic requirements of any plant you choose to study? Can any one of these substances be replaced by two or more other substances?

What inorganic or organic compounds are inimical to a plant you select for study, and how can the adverse effects of such agents be minimized? Explain the results you obtain, and test your explanation by further experimentation.

How does a plant assimilate nutrients through the membrane covering its roots? Test your explanation by further study.

Transformation of Organic Compounds by Microorganisms

See PERLMAN, D., *J. Chem. Educ.*, **36**, 60–3 (1959).

The best known chemical reaction commonly attributed to microorganisms is the fermentation of sugars to ethyl alcohol, though this is by no means a unique phenomenon. The preparation of sauerkraut from cabbage, of silage for animal feed, of cheeses from milk, are other common examples. But in addition to these, the production of large, industrial quantities of many chemical reagents depends upon the action of microorganisms. For example, gluconic acid, sorbose, lysine, butanol, acetone, and citric acid have been or are now produced by microorganisms. Further, though not yet commercially exploited to a great extent, microorganisms can be used for other purposes such as the introduction of hydroxyl groups into a desired position on a large molecule, removal of hydrogen from selected positions, oxidation of a hydroxyl group to a ketone, and many others.

Similar information, though less up to date, can also be found in DUNN, C. G., *J. Chem. Educ.*, **19**, 387–92 (1942).

Neither article gives sufficient detail for students to use directly in their studies of microorganisms as chemical agents. Some supplemental reading in other sources and some preliminary laboratory studies will be necessary.

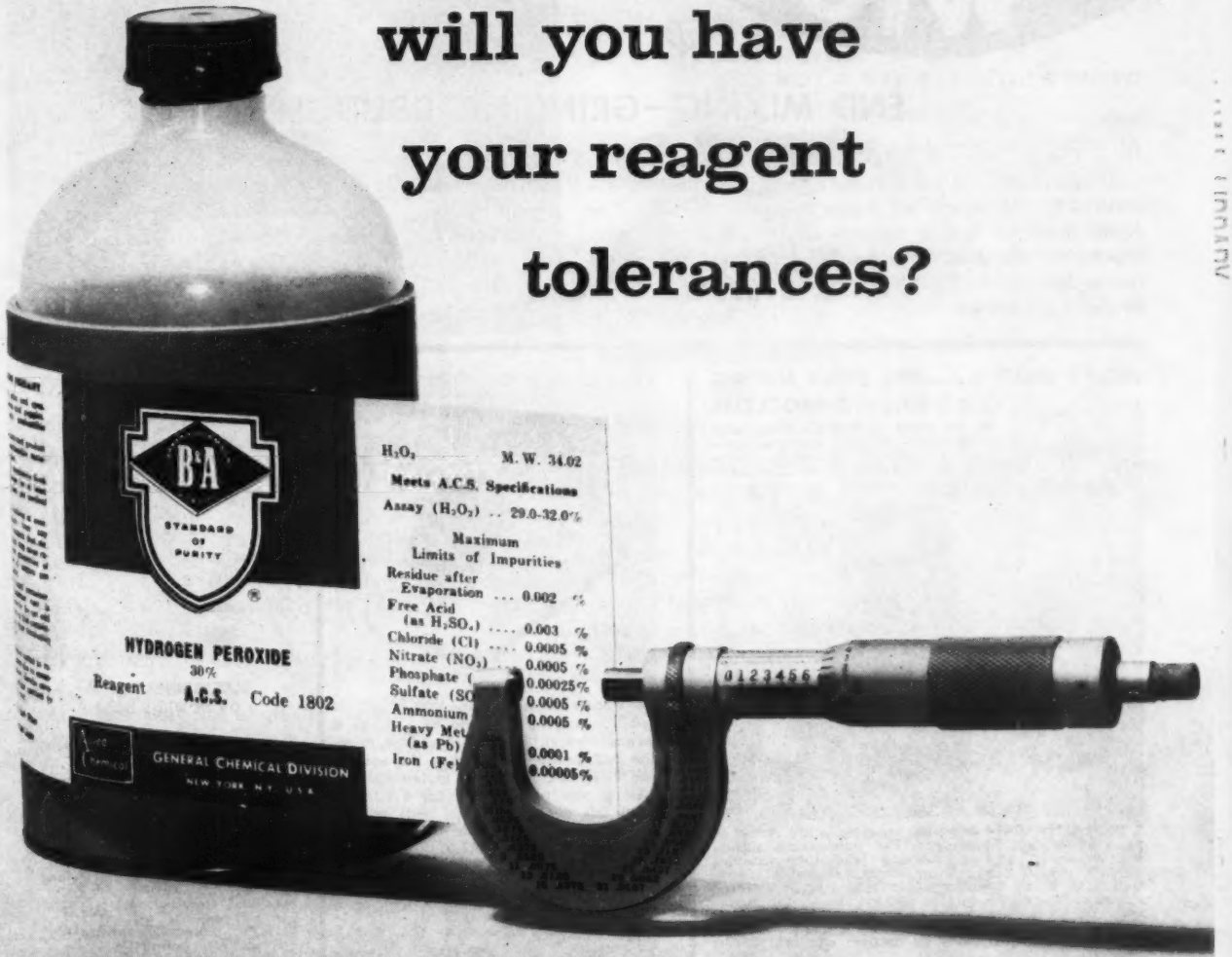
A few of the microorganisms that can be used as chemical agents are pathogenic. Therefore, the supervision of a competent biologist during the planning stages and during laboratory work periods is desirable. A simple device for pipetting pathogenic organisms is described by GHOSH, D., *J. Chem. Educ.*, **36**, 76 (1959).

A differential fermentograph, which may be useful in some investigations, is described by BORZANI, W., AND VAIRO, M. L. R., *J. Chem. Educ.*, **36**, 242 (1959).

Question:

Show that an organic compound, which you select, can be produced by a microorganism, that an organic compound produced by a microorganism can be used as an intermediate in the synthesis of another organic compound, or that an oxidation, deamination, demethylation, or other type of reaction can be controlled by the use of a suitable microorganism. Determine that a pure strain of the microorganism you use is, or is not, necessary for your purposes. Determine the optimum conditions for the microbial activity you desire to encourage.

How precise will you have your reagent tolerances?



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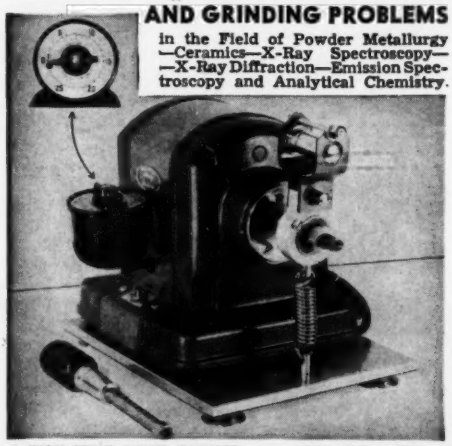

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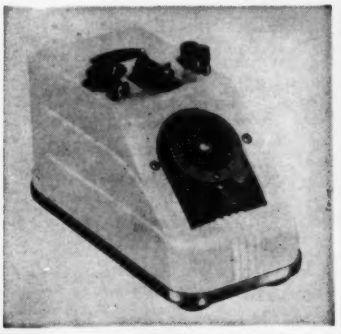

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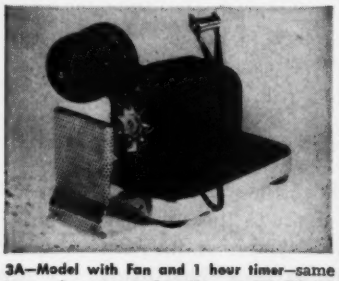

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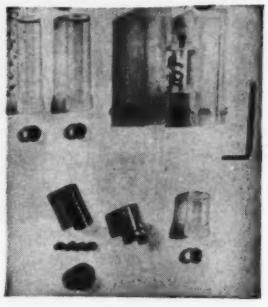

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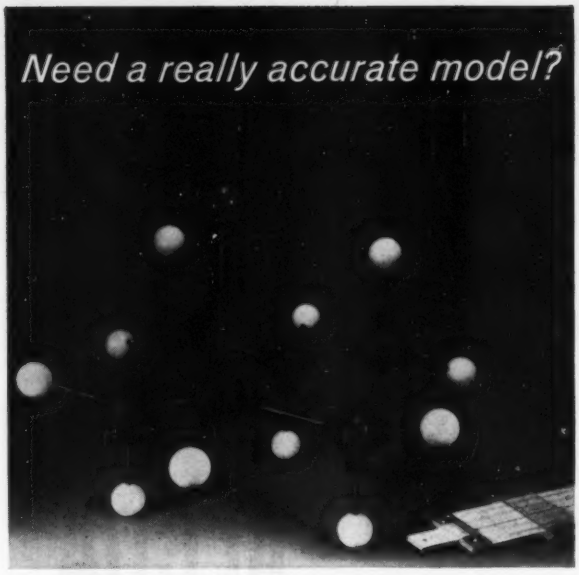

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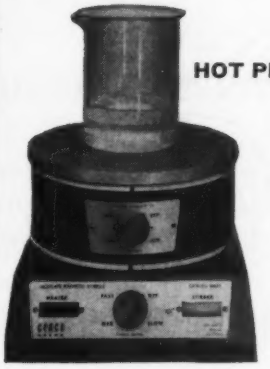

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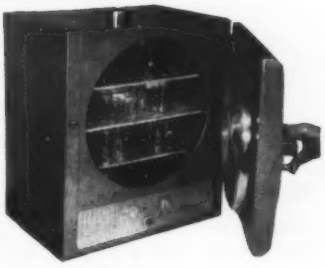

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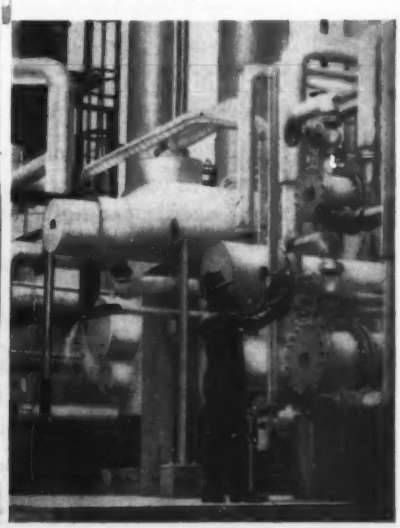

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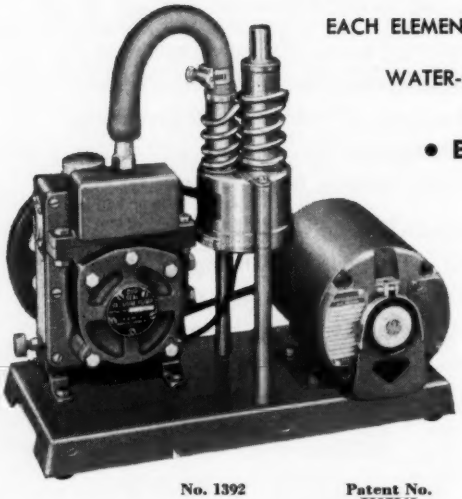

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Chem Ed

EDITORIALLY SPEAKING

EDITOR'S NOTE: It is most appropriate for this page to remind readers of significant chemical anniversaries. Sesquicentennials are relatively few. 1961 is such a year for the famous but long-neglected proposal by Avogadro. At the editor's request, Professor Aaron J. Ihde, a member of the Editoral Board, has prepared the following remarks. We commend them to readers of this page as an excellent example of how a historical perspective can help clarify the view of the future.

Certain developments in the history of science are sufficiently noteworthy that they deserve periodic reexamination. Avogadro's hypothesis, published in 1811, is such a case. On this 150th anniversary of the occasion we are all aware that chemistry has progressed far since the Italian lawyer made his suggestions. Some of this progress can certainly be credited to application of the hypothesis. Yet we often forget that the hypothesis, for all of its fruitfulness, was virtually ignored for 50 years—and that this 50 years was an extremely chaotic one in chemistry. How can such an important tool be overlooked for such a lengthy period? And are we today overlooking concepts which are equally important to our present day problems?

The atomic theory was introduced to the chemical world in 1808 with the publication of Dalton's "New System of Chemical Philosophy." Gay-Lussac's paper leading to the Law of Combining Volumes, published in 1809, should have served to strengthen atomic concepts, but rather it raised new questions which failed to correlate with experimental observations. Dalton could never agree that the Gay-Lussac whole-number ratios in gaseous reactions were more than fortuitous; nay, he even argued that Gay-Lussac's figures were in error.

Avogadro recognized that Dalton's theory and Gay-Lussac's law might be reconciled if the molecules of elemental gases were treated as polyatomic. In his paper, published in the *Annales de chimie et de physique*, he showed that theory and experiment were in agreement if molecules of hydrogen, nitrogen, and oxygen were treated as diatomic. However, as often happens in science, other knowledge shows that a proposed hypothesis cannot be accepted. Had electrochemistry not been a red-hot subject at the moment, Avogadro's hypothesis might have found a more sympathetic following. The belief that chemical affinities must be electrical appeared to rule out the idea of atoms with like polarities existing in stable diatomic molecules. Without the support of Dalton, Davy, and Berzelius, Avogadro's hypothesis was doomed to neglect. Even the independent reintroduction of the idea by Ampère in 1814 could not gain for the hypothesis a sympathetic reexamination.

It is frequently alleged that the hypothesis failed to gain acceptance because Avogadro's paper was highly mathematical and otherwise ambiguous. Anyone who will consult the readily available *Alembic Club Reprint No. 4* containing Avogadro's paper will see that this explanation is invalid. The failure lies rather in the generally confused state of chemistry in the first half of the 19th century. A discipline with growing pains is sure to ignore useful concepts which appear before their significance is obvious. One can think of Semmelweiss and his ideas on contagion, of Mendel and his studies on inheritance. Possibly nuclear science, with its 30-odd sub-atomic particles, is today in its messy state because the "Avogadro's hypothesis" which will clarify it is being ignored.

It is also of interest to recall that the revival of Avogadro's hypothesis came about as the consequence of a chemistry teacher's difficulty in making his subject comprehensible to his students. In searching for a unifying principle, Cannizzaro recognized it in 1858 in his countryman's forgotten hypothesis. His classroom success in use of the hypothesis gave him the courage to appear before the Karlsruhe Congress to advocate application of the hypothesis to those problems which had kept chemistry in a state of confusion. In an era when it is fashionable to believe that all progress is made through single-minded attention to experimental research, we may pause to reflect that those who seek to clarify the teaching of chemistry can also make important contributions.

AARON J. IHDE
UNIVERSITY OF WISCONSIN, MADISON

H. Tracy Hall
Brigham Young University
Provo, Utah

The Synthesis of Diamond

Ever since Antoine Lavoisier in 1792 and Smithson Tenet in 1797 demonstrated that diamond and graphite are allotropic forms of carbon, man has been interested in converting the relatively abundant graphite into the much rarer diamond. Success in this endeavor, however, has only been achieved in recent years, and tiny crystals about $^1/_{10}$ mm average diameter, valued at about $6000 per pound, are being quantity produced in direct competition with natural diamonds. These diamonds are used primarily in diamond grinding wheels.

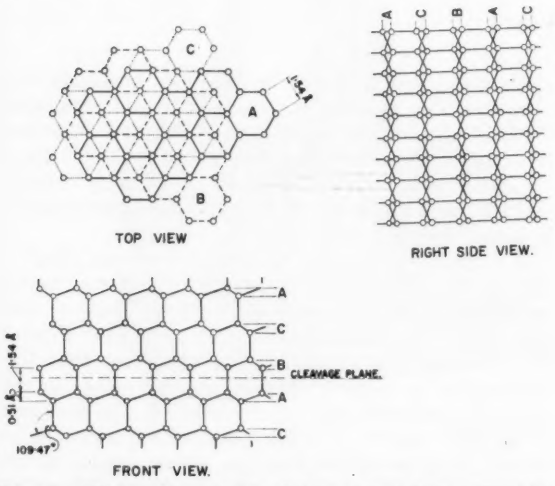


Figure 1. Orthographic projections of diamond space lattice. For aid in visualization, the hexagonal rings of layer A are outlined with solid lines in the top view. Layer B hexagons are outlined by dashes, and layer C hexagons with dots.

Crystal Structure Information

The differences between graphite and diamond at the atomic level were not known until after X-ray diffraction techniques for the elucidation of crystal structures were developed during the 1910–20 decade. Diamond, one of the earliest crystals studied, was shown to consist of carbon atoms arranged in puckered, hexagonal rings lying approximately in the 111 crystallographic plane. (This is the natural cleavage plane of diamond.) These sheets of hexagonal, puckered rings are stacked one above the other in sequences such that atoms in every fourth plane duplicate the position of atoms in the first. By analogy to closest packings, this sequence is designated . . . abcabc . . . . In this structure every carbon atom is surrounded by four other carbon atoms equidistant from the central carbon atom at angles of 109°28′ (the tetrahedral angle) from each other (see Fig. 1).

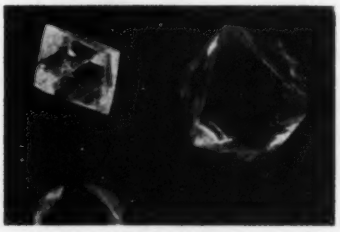
The arrangement of atoms in crystals of graphite is similar to that of diamond in that it consists of a parallel stacking of layers comprised of carbon atoms forming hexagonal rings. The hexagonal rings in graphite, however, are probably only very slightly puckered. The classical graphite structure indicates an . . . abab . . . stacking sequence for the layers (atoms in alternate layers occupy equivalent positions). According to some interpretations of the electron diffraction patterns given by graphite, the . . . abcabc . . . configuration (Fig. 2) is present to an appreciable extent in graphite, (*1*, *2*). As with diamond, the cleavage plane is parallel to the stacked layers. However, graphite is cleaved with extreme ease compared to diamond.

In diamond, all distances between atoms are 1.54 Å. In graphite, the inter-atomic distances within a layer are all equal (1.42 Å). Individual planes in the graphite lattice, however, are spaced far apart (3.37 Å). This immediately suggests that the bonding within the planes is different from the bonding between atoms of neighboring planes. It is thought that the bonding between planes in the graphite crystal is of the van der Waals type.

Although the accepted ideas of the crystal structure for diamond have not changed since the earliest determination, there have been periodic questions concerning details of the crystal structure of graphite, and these questions continue to the present day. There is no doubt, however, that the essential features of graphite are those of approximate hexagonal rings of carbon atoms arranged in layers separated a considerable distance apart relative to the distance between adjacent carbon atoms in the hexagonal rings.

To further characterize the differences on the atomic scale between graphite and diamond, it is necessary to look into the nature of the bonding between atoms. In diamond, the bonding is predominantly covalent in

The cover



The photomicrograph on the cover shows a collection of diamonds synthesized by the author at Brigham Young University. An idea of their actual size can be established by noting that the vertical dimension of the largest crystal (the upper right) in the photograph here reproduced is approximately 0.2 mm.

It is difficult to take still photographs of diamonds. The brilliance is observed best when either the diamond, the light source, or the camera is in motion.

nature and is due to the formation of sp^3 hybrid bonds. All bonds within diamond are equivalent and are "aliphatic" in character. The bonds between carbon atoms in the hexagonal rings in graphite apparently have some double bond character. Therefore, the entire layer or sheet consists of a giant, two-dimensional resonating molecule—a molecule that is somewhat "aromatic" in character (*3*, *4*).

Because of the similarities in crystal structures, a cursory examination might lead to the conclusion that graphite could be converted to diamond by brute force; i.e., by applying sufficient pressure, the bonds between

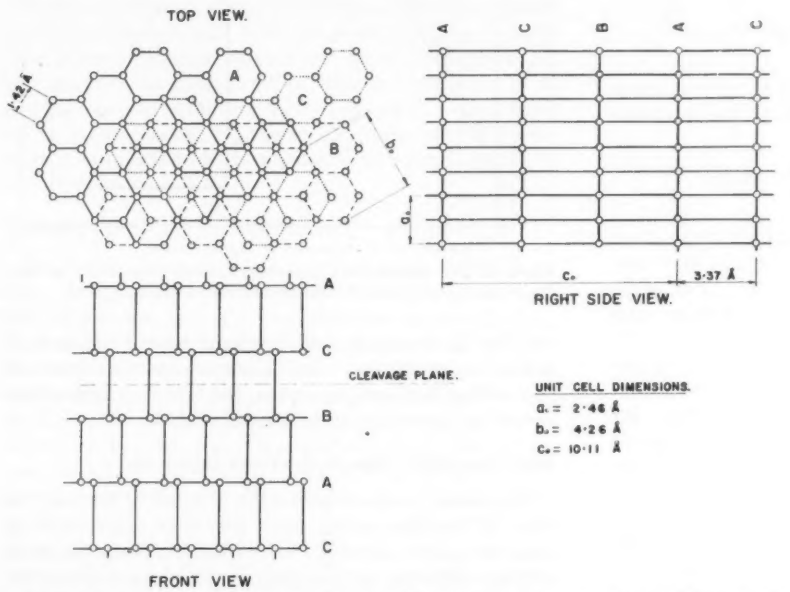


Figure 2. Orthographic projections of rhombohedral graphite space lattice. Scale is the same as that used in Figure 1.

graphite layers would be shortened the proper amount and the hexagonal carbon rings would be forced to "pucker," the whole process causing the atoms to conform to the diamond crystal lattice. The years have shown, however, that there are some complicating factors in this direct conversion of graphite to diamond.

Thermodynamics and Kinetics of Conversion

A modern day chemist knows that he must be concerned with two problems whenever he wants to bring about a chemical change. (A change from one polymorphic form to another may be regarded as a type of chemical change.) He must first consider the *thermodynamic* problem and second, the *chemical kinetic* or *reaction rate* problem. Chemical thermodynamics is concerned with the relative energies of the reactants and the products of a chemical reaction. Under conditions where the free energy of the reactant(s) F_r is greater than the free energy of the product(s) F_p, the relative energy $F_p - F_r = \Delta F$ is negative and the reaction has thermodynamic permission to proceed toward formation of the products. In the case at hand, the reactant is simply graphite and the product is diamond: $C_{graphite} = C_{diamond}$. On the other hand, if ΔF is positive, the reaction has thermodynamic permission to proceed in the opposite direction; i.e., the products (as the reaction is written) will proceed to transform into the reactants. Under conditions where ΔF is zero, a stalemate (equilibrium) exists and there is no net tendency for the reaction to proceed in either direction.

Thermodynamics does not give any information about the time required for a reaction to take place. The ΔF may, in many instances, have a large negative value, yet the reaction is found to proceed at an imperceptible rate. An oft quoted example of this situation is the bulb containing a mixture of hydrogen and oxygen gases. For the reaction, $H_2 + {}^1/_2\ O_2 = H_2O(g)$, the standard change in free energy is $-55{,}600$ cal. Nevertheless, the bulb may be kept for many years without detecting the formation of any water vapor.

It is the business of chemical kinetics to deal with the rates of chemical reactions. For this purpose theories and techniques for understanding the atomic and molecular processes (reaction mechanisms) taking place in chemical reactions have been developed. Application of the theory, coupled with appropriate experiments, often points the way toward finding means of increasing or decreasing the rate of a given reaction.

Favorable Negative ΔF as Pressure Increases

For the reaction $C_{graphite} \rightarrow C_{diamond}$, $\Delta F° = +692$ cal/g-atom at 25°C and 1 atmosphere pressure (*5*). This $\Delta F°$ is not obtained by direct measurement but, as is the case with most thermochemical data, is calculated from measurements of heats of combustion, specific heats, compressibilities, thermal expansions, etc. The positive $\Delta F°$ indicates that diamond is thermodynamically unstable with respect to graphite. However, diamonds have not been known to transform into graphite by any observable amount over periods of hundreds of years under ordinary conditions. The rate of reaction (conversion) must, therefore, be extremely slow. Increased temperature will accelerate most reactions and this is also true for the conversion of diamond to graphite. This transformation begins to proceed at an observable rate at a temperature in the neighborhood of 1200°C at 1 atm. At this pressure and temperature $\Delta F°$ has increased to about +2400 cal indicating that higher temperatures decrease the thermodynamic stability of diamond. The $\Delta F°$ for the graphite-diamond transition assumes its lowest value at the the absolute zero of temperature

$$\Delta F_0° = +580 \text{ cal/g-atom at 1 atmosphere}$$

In order to bring the graphite-diamond reaction into

a region where $\Delta F°$ is negative, it is necessary to apply pressure. The pressure required depends on the temperature—the higher the temperature, the greater must be the pressure.

Equilibrium is established when the free energy difference between the two allotropes is zero, i.e.,

$$\Delta F = \Delta H - T\Delta S = 0$$

The manner in which ΔF varies with pressure at a given temperature is given by

$$\left(\frac{\partial \Delta F}{\partial P}\right)_T = \Delta V$$

or by

$$\Delta F_T{}^P - \Delta F_T° = \int_0^P \Delta V dP$$

where ΔV is a function of both T and P. From these expressions the free energy difference at any pressure and temperature may be expressed as

$$\Delta F_T{}^P = \Delta H_T° - T\Delta S_T° + \int_0^P \Delta V dP$$

Data is available for evaluating $\Delta H_T°$ and $\Delta S_T°$ to 1200°K. Evaluation of the integral, however, involves some reasonable approximations. For additional details, the reader is referred to Berman and Simon (*5*).

A graph showing the approximate pressure-temperature relationship is shown in Figure 3. The line represents the pressure and corresponding temperature for which $\Delta F° = 0$. Above the line $\Delta F°$ is negative and diamond is the stable carbon allotrope. Conversely, graphite is stable in the positive $\Delta F°$ region below the line.

Graphite, subjected to P-T conditions above the line, should transform to diamond. Graphite has been subjected to conditions lying approximately below the solid line of Figure 4. Although part of this area overlaps the diamond stable region, diamond has not yet been observed to form directly from graphite under these conditions. Since the thermodynamic

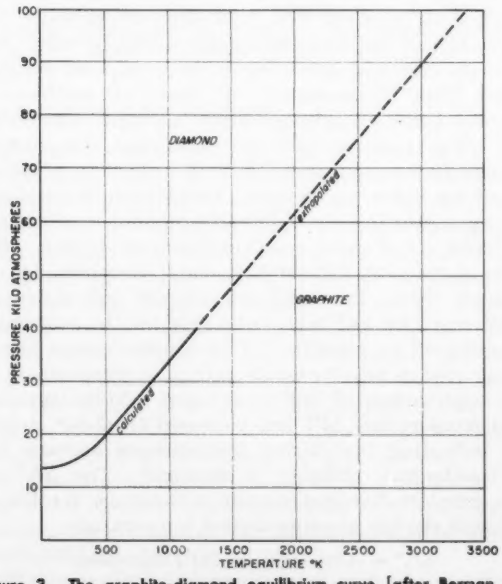


Figure 3. The graphite-diamond equilibrium curve [after Berman and Simon (*5*)].

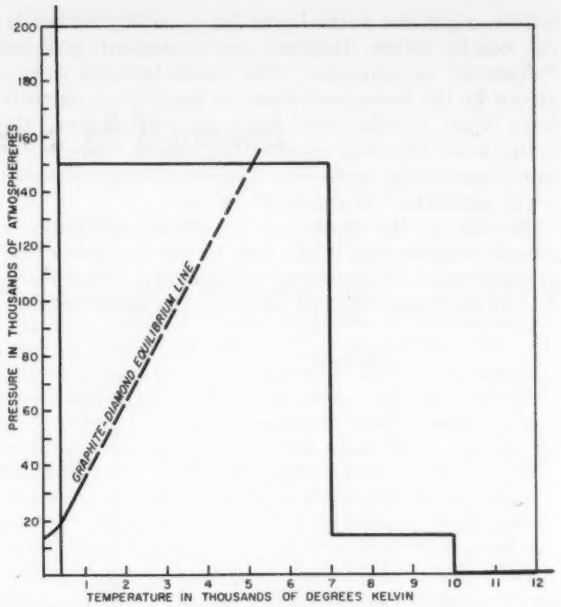


Figure 4. The approximate pressure-temperature conditions to which graphite has been subjected (area below the solid line).

criteria for formation of diamond have been met, it must be concluded that kinetic considerations are controlling and are preventing the transformation from occurring in any practical length of time.

Less Favorable Rate as Pressure Increases

Increased temperature might ultimately increase the rate of transformation to a practical value, but increased temperature (to stay within the diamond stable region) calls for an increase in pressure beyond the range of the high pressure devices currently available.[1] At this impasse an investigation of the rate process is enlightening. Although diamonds cannot yet be made by direct conversion from graphite, graphite can easily be made from diamond. Studies of this reverse transformation under high-pressure, high-temperature conditions can give information concerning the reaction mechanism.

Experiment shows that high pressure retards the rate of transformation of diamond to graphite. The theory of absolute reaction rates indicates for such a situation (*6*) that

$$\log \text{rate} = \text{constant} - \frac{\Delta V^{\pm} P}{RT}$$

where $\Delta V^{\pm}$ is the molar difference in volume between diamond and the activated complex (the intermediate state or transition state), P is the applied pressure, T is the temperature, and R is the molar gas constant. Although available experimental data are somewhat erratic, a plot of log rate versus P leads to the inescapable conclusion that $\Delta V^{\pm}$ is at least 10 cc. Note that the molar volume of diamond is 3.42 cc, the molar

[1] Note added in proof: DeCarli, P. S., and Jamieson, J. C., *Science*, **133**, 1821 (1961), have just reported the synthesis of eight-micron-diameter diamonds directly from rhombohedral graphite by means of an explosive shock. Transient pressure was estimated to reach 300,000 atm. An estimate of the temperature achieved was not given.

volume of graphite 5.34 cc, and their difference in molar volume ΔV is only 1.92 cc. Obviously the transition state, with a molar volume $V^{\pm}$ of at least (10 + 3.42) cc is a very open or expanded structure. It is reasonable to assume that the transition state for graphite-diamond conversion is the same as for the formation of graphite from diamond. This being the case, there arises the very frustrating but extremely interesting situation that higher pressure leads to more favorable thermodynamics (a more negative ΔF) for the conversion of graphite to diamond, but, at the same time, leads to less favorable reaction kinetics since it suppresses the formation of the expanded activated complex. At the pressures and temperatures to which graphite has been subjected, to the present time, reaction kinetics apparently have the upper hand and prevent the synthesis of diamond directly from graphite in any practical period of time. Additional information concerning thermodynamics and reaction rates, as applied to high pressure reactions, is set forth in reference 7.

Success: Graphite → Diamond

From the above analysis it would seem desirable to take the graphite lattice apart atom by atom and build the atoms one at a time into the diamond lattice. This might be accomplished by means of a solvent. Conceivably the proper solvent would take carbon atoms from graphite into solution as individual entities which, under the influence of proper thermal and concentration gradients would migrate through the solvent and precipitate as diamond. Nature gives some clues as to possible solvents. Diamonds are found imbedded in ferro-magnesium silicates, from which they apparently crystallized, in the famous pipe mines of South Africa. A few diamonds have been found embedded in iron-nickel and in troilite (FeS) constituents of meteorites (*8*).

My first synthesis of diamond was based on the idea that diamonds might be crystallized from troilite. On December 16, 1954, at the General Electric Research Laboratories in Schenectady, New York, I performed an experiment in the "Belt" high pressure, high temperature apparatus with a cell arrangement as shown in Figure 5.

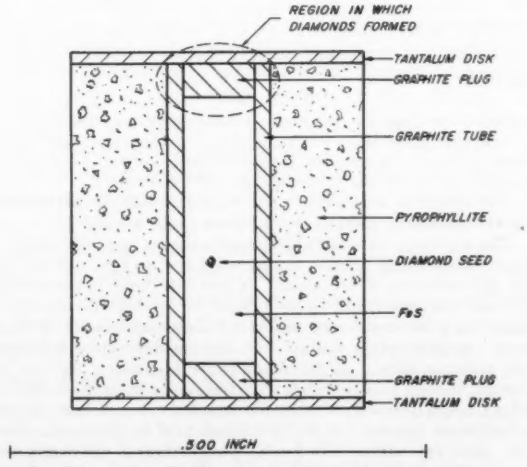


Figure 5. Cross-section of cell in which first diamonds were grown.

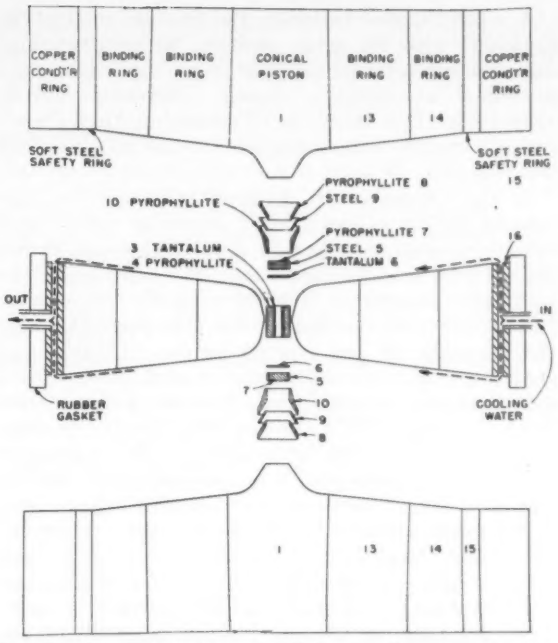


Figure 6. The "Belt" high-pressure, high-temperature apparatus, "exploded" view.

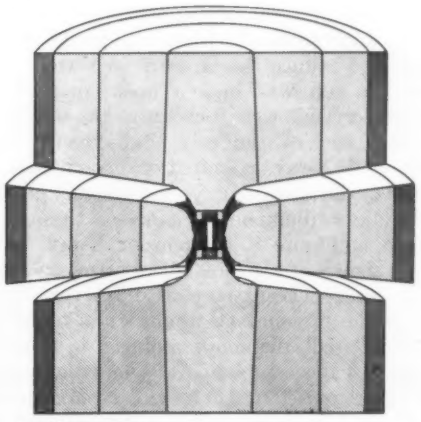


Figure 7. "Belt" apparatus.

A brief diversion is necessary at this point to make a few comments concerning the apparatus. The "Belt" apparatus makes use of two opposing, conical pistons thrust into opposite ends of a symmetrical, tapered chamber (Figures 6, 7). Relative motion of the pistons with respect to the chamber is afforded by a compressible gasket. The solid pressure transmitting material used in the device serves also as electrical and thermal insulation. The design allows pressures greater than 100,000 atm to be continuously maintained simultaneously with temperatures above 2500°C. (Temperatures estimated to be as high as 7000°K have been maintained for a few seconds.) Development of this device opened a large, hitherto inaccessible thermodynamic region to scientific exploration. The relative simplicity of the design has made it an extremely useful and practical tool. (The theory of its operation and details concerning use, design, and development are to be found in references *9*, *10*, *11*, and *12*.)

A second device (actually the first to be publicly disclosed) with the same pressure, temperature, and diamond synthesizing capabilities as the "Belt" was developed at Brigham Young University during 1956–1957. It is called the "Tetrahedral Anvil Press" and is currently finding considerable use as a research tool (*13*).

In the December 16 diamond synthesis run, the tapered pistons of the "Belt" apparatus were forced into the loaded chamber by a 223,000-pound thrust delivered by a hydraulic press. After one minute the load was reduced to 186,000 pounds. An electric current (60-cycle, alternating) was then passed through the assembly via the tapered pistons. Current was gradually increased over a period of 6 minutes to a maximum value of 346 amps. The voltage drop across the pistons was 1.84 v corresponding to a power dissipation of 636 w. The temperature inside the graphite tube at this power level was approximately 1650°C. The pressure, at the time, was thought to have been in the neighborhood of 95,000 atmospheres. There has been some controversy over the calibration of high pressure apparatus recently, however, that would place the actual pressure as much as 20% below this figure. Even assuming the lower pressure value, however, the system was in a region of thermodynamic stability for diamond. Maximum temperature was maintained for about three minutes, after which it was lowered to room temperature in approximately five minutes. After the temperature had been lowered, 18 minutes were taken to reduce the pressure to 1 atm.

When the cell was broken open, dozens of tiny transparent crystals were found near the tantalum disc at the top end of the cell. Subsequent chemical, physical, and X-ray examinations conducted during the course of the next few days conclusively proved that the material was diamond. Pictures of these diamonds are shown in Figure 8. A powder X-ray diffraction pattern is shown in Figure 9 where arrows point to the diamond lines. The extraneous diffraction lines were caused by the presence of graphite and tantalum carbide. The "seed" diamond employed in this run was unchanged at the completion of the experiment. No new diamonds were found in its vicinity and subsequent runs without a diamond seed were successful.

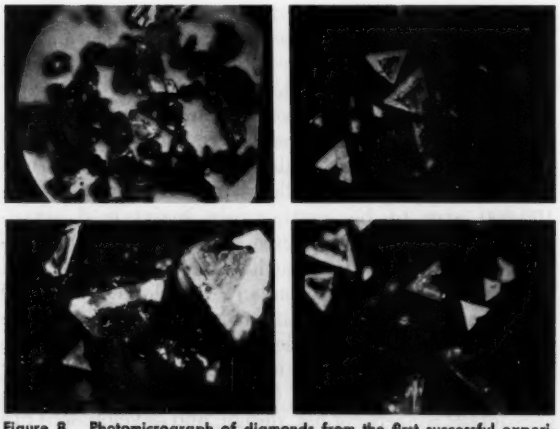


Figure 8. Photomicrograph of diamonds from the first successful experiment, Dec. 16, 1954.

During the period December 16 through December 31, 1954, I performed 27 high pressure experiments similar to the successful December 16 experiment with some changes in the various experimental parameters. Diamonds were made in 12 of these runs. Since FeS was known to be a non-stoichiometric type compound, usually with excess iron (Fe_xS where $x > 1.00$), pure iron was substituted for the FeS and diamonds were successfully grown in that solvent. Substitution of pure sulfur for FeS did not produce diamonds. Microscopic examination of the cell contents following a run with FeS or Fe disclosed that a black coating (removable by acid) covered the diamonds. Carbon atoms, derived from graphite or metallic carbides formed in the reaction mixture, apparently migrate through this film and precipitate as diamond. The film is probably iron. The tantalum (or more particularly tantalum carbide) which formed in the presence of carbon, seemed to aid diamond growth.

Of practical importance in locating the correct temperature for diamond formation was my observation that onset of diamond growth was signalled by a drop in heating current through the sample and a corresponding rise in voltage across the sample. As heating power was controlled by a variable auto transformer, it was only necessary to increase the power output of the transformer until this phenomenon took place.

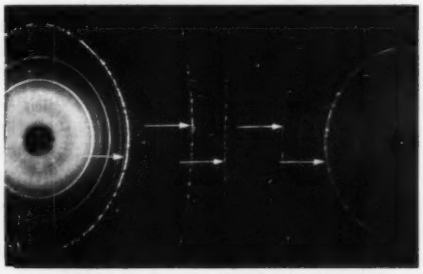


Figure 9. X-ray diffraction. Powder photographs of some of the diamonds from the first successful synthesis experiment (CuK_α radiation). Arrows point to the diamond lines.

The power setting was then left unchanged for 2 or 3 minutes until diamond growth was about complete.

On December 31, 1954, Dr. H. Hugh Woodbury of the General Electric Laboratory duplicated my December 16 run and thus, to our knowledge, became the first man to duplicate the diamond synthesis claim of another.[2]

[2] At this point it was evident that a landmark in science had been reached. In reaching that landmark, I could take particular satisfaction in the following key contributions:

The design of the "Belt" apparatus that made experiments in the 100,000-atm, 2500°C-temperature range possible.

The discovery of a suitable combination of pressure, temperature, chemical ingredients, timing sequence, and cell arrangement for the synthesis of diamonds. It was extremely important that (*a*) the synthesis could be reproduced by myself and others; (*b*) diamond growth was very rapid; (*c*) diamond yields were significant—outstripping a million fold the concentration, relative to the growing matrix, of diamonds found in nature; (*d*) the diamonds, though tiny (crystals with triangular faces up to 300 μ on edge), could be observed with the unaided eye and were obtained in sufficient quantity to be "felt" and held in the hand. Items (*b*) and (*c*) above obviously foreshadowed the commercial production of diamond.

Simple substitution of other transition metals for iron subsequently showed that many of these elements were suitable solvents for the synthesis of diamond.

By February 15, 1955, diamonds had been produced in about 100 separate runs in the General Electric Research Laboratory. On this date a press conference was held and the fact that diamonds had finally been made by man was announced to the world. However, details concerning the synthesis were not released. On October 22, 1957, the company announced that diamond production had successfully been carried through the pilot plant stage—more than 100,000 carats (a carat = 0.200 gram) having been produced up to that time. Thus, less than three years following the successful conclusion of a 100-plus years' search for a method to convert ordinary black carbon into diamond, man-made diamonds became a commercial product. Details of apparatus and methods of synthesis were finally released in the fall of 1959.

Following the February 15, 1955, synthesis announcement by the General Electric Co., several claims to prior synthesis were voiced. Only one of these claims has appeared in a technical journal. It appeared as an article entitled "Artificial Diamonds" by H. Liander in the *ASEA* (*Allmänna Svenska Elektriska Aktiebolaget*, Västerås, Sweden) *Journal* for May-June of 1955. The method of synthesis was not given but the statement was made that "ASEA produced its first diamonds on 15th February, 1953." The experimental procedures used were disclosed in 1960 and were similar to those used at General Electric (*14*).

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George B. Smith, C. A. Hollingsworth, and **Darl H. McDaniel**
University of Pittsburgh
Pittsburgh, Pennsylvania

Solvation and Association from Colligative Properties by Graphical Means

There have been numerous examples in the literature of the application of Raoult's law to colligative property data to determine the molecular weight, or the apparent molecular weight, of the solute. In many cases the apparent molecular weight was found to be concentration dependent. Such a variation of the apparent molecular weight with the concentration may be an indication of solvation and/or association of the solute molecules, or it may be the result of non-ideality which cannot be described in such specific terms. It was the underlying assumption of the so-called "chemical" theory of solutions as proposed and applied long ago by Dolezalek (*1*) that all non-ideal behavior of solutions can be described by the application of Raoult's law when the proper solute species is used. It is now recognized (*2*) that the "chemical" picture is often inadequate because it does not properly take into account non-specific energies of interaction (i.e., interactions of the van der Waals type) and entropy effects caused by non-random mixing or differences in the molecular shapes and sizes of the components (*2*). For example, the separation of a mixture into two liquid phases cannot be explained in terms of an ideal mixture of solvent and a reasonable solute species, or mixture of solute species. Nevertheless, the chemical picture should be a reasonable approximation for systems in which the predominate interactions are those of a specific type, such as the Lewis acid-base interactions.

Thus in some cases the chemical theory can be useful. One case, which will be mentioned only briefly here because data other than the colligative property data are required (cell voltages, for example) is that of the

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complex hydrolysis equilibria of some metal ions in aqueous solutions (*3*). In these solutions the effect of ideal behavior is assumed to be achieved by the addition of an inert electrolyte, such as sodium perchlorate, in sufficient quantity to maintain a constant ionic strength, which in turn, presumably, causes the activity coefficients to remain constant.

In non-aqueous systems it is probably not possible to disentangle the effects of the non-ideal entropy of mixing and the non-specific interactions mentioned above on the one hand from the effects of a series of equilibria of solute-solvent and/or solute-solute complexing reactions on the other. Although equations have been derived for such cases (*2*, *4*), results of their application to colligative property data do not lead to clear-cut conclusions about the formulas for the solute species (*5*).

Because of the saturation nature of acid-base interactions one would expect that in many cases the solute should exist as a single solvated and/or associated species. In such cases it may be possible to determine the solute species from a colligative property even when there is some non-ideality caused by non-specific interactions. In this connection it is desirable to have a method which is free from preconceived notions concerning the solute species. Prejudice is obviously inherent in the frequently used method of trial and error by which one tries various possible formulas until a formula is found which leads to a molecular weight which appears not to be too concentration-dependent.

It is the purpose of this paper to present some convenient graphical methods for treating colligative property data to identify the solute species, provided the solute exists as a single species.

Outline of the Methods and Examples

Let the solute species be represented by the formula A_kB_l, where k and l are integers, but in what follows they will be treated as though they were continuous variables. The mole ratio, defined as the moles of free solvent B per mole of solute A_kB_l, is given by

$$\theta = \frac{I - (l/k)}{(1/k)} \tag{1}$$

where I is the ratio of the total moles of solvent B, bound and unbound, to monomeric formula weights of solute A. θ is given in terms of colligative properties by Raoult's law.

Equation (1) can be rearranged for plotting in several different ways. For example, in the form

$$\frac{l}{k} = -\frac{\theta}{k} + I \tag{2}$$

a plot of l/k versus $1/k$ is a straight line with intercepts I and I/θ. The value of I depends on the composition of the solution only, and in terms of the molality, m, based on the monomeric solute, is given by

$$I = 1000/mM_1 \tag{3}$$

where M_1 is the molecular weight of the solvent. I/θ is the ratio of the measured value of the colligative property to the ideal value based on the monomeric, unsolvated solute. For example, in terms of boiling-point elevation, freezing-point lowering or the practical osmotic coefficient, respectively,

$$I/\theta = \Delta T_b/mK_b = \Delta T_f/mK_f = \phi \tag{4}$$

where K_b and K_f are the molal boiling-point and freezing-point constants. I/θ can also be interpreted as the monomeric formula weight of the solute divided by the apparent molecular weight calculated in the usual fashion. By using these intercepts it is easy to plot a family of lines, one line for each concentration and corresponding value of the colligative property. A single species is indicated if these lines have a common point of intersection, and the formula for the solute species is given by the values of l/k and $1/k$ at the point of intersection.

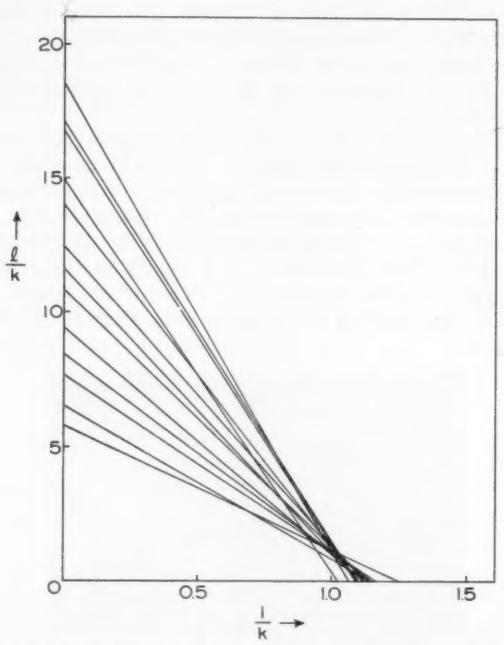

Figure 1. Lines for the $GaCl_3$–CH_3Cl system from vapor pressures at −78.5°C.

Examples of this type of plot are shown in Figures 1, 2, and 3. The data for the methyl chloride-gallium trichloride system are those given by Brown, Eddy, and Wong (*6*). Their conclusion that the solute

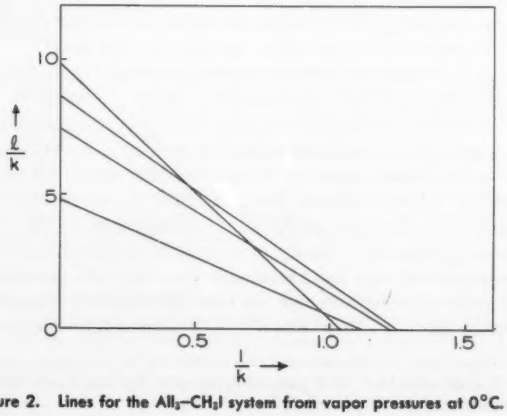

Figure 2. Lines for the AlI_3–CH_3I system from vapor pressures at 0°C.

species in solution is $CH_3ClGaCl_3$ is confirmed by Figure 1. The lines in Figure 2 were obtained from the data given by Brown and Wallace (*7*). This figure shows agreement with the conclusion made by Brown and Wallace that these data indicate monomeric aluminum iodide. However, the belief expressed by Brown and Wallace that these data favor the existence of a 1:1 complex between solute and solvent is not confirmed by Figure 2. The lines for the benzene-aluminum bromide system were obtained from vapor pressures at 17.7° C (*8*). The unsolvated dimer Al_2Br_6, with perhaps slight dissociation, is indicated.

Another interpretation of equation (1) or (2) is obtained by changing its form to

$$\theta = kI - l \qquad (5)$$

and treating θ and I as variables with k and l constant. In this form all of the data for a given system lie on the same θ versus I curve. When the solute is a single species obeying Raoult's law this curve is a straight line with a slope equal to k and a θ-intercept equal to $-l$. Plots of this type for the examples considered in the previous paragraph are shown in Figure 4. One disadvantage of this method as compared to the use of the family of lines is revealed by considering the case of the methyl iodide-aluminum iodide system. From Figure 4 one would probably conclude, in agreement with Brown, *et al.* that there is evidence for a 1:1 complex. However, it is clear from Figure 2 that such a conclusion is not justified. Thus, although there is little to choose between the two methods with respect to ease of application, it would appear that the use of the family of lines is to be preferred, because they are less likely to lead one to unwarranted conclusions.

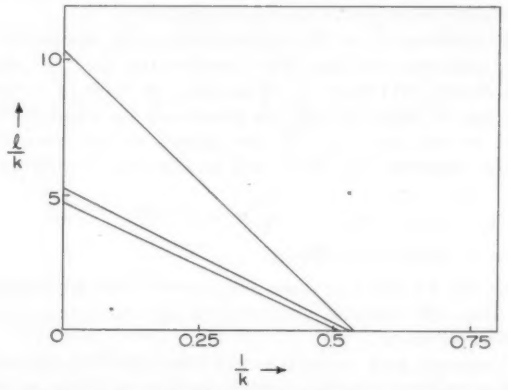

Figure 3. Lines for the $AlBr_3$–C_6H_6 system from vapor pressures at 17.7°C.

A third variation of the treatment is to use equation (5) in the form

$$l = kI - \theta \qquad (6)$$

with I and θ treated as constants and l and k as variables. This is essentially the same treatment as that described for equation (2). Although the graphs of equation (6) are easier to interpret than those of equation (2), the graphs of the latter equation as illustrated by Figures 1–3 may be a little easier to construct.

These examples illustrate what might be called a "valuable perspective" from which to view the problem of defining the solute species. Graphical methods can put colligative property data in a form which strongly suggests an appropriate formula for the solute. However, it must always be borne in mind that any treatment such as this assumes the validity of Raoult's law for the solute-solvent system. Consequently, the whole argument rests on the presupposition that an ideal solution exists. All of this may lead to strong evidence in favor of solute species postulated to agree with the colligative property data, but it is not proof.

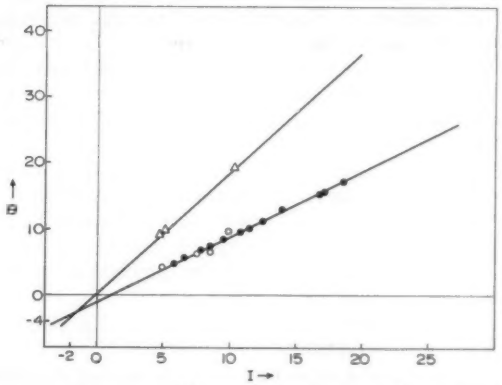

Figure 4. Test of equation (5) for systems $GaCl_3$–CH_3Cl (●), AlI_3–CH_3I (○) and $AlBr_3$–C_6H_6 (Δ).

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Chem Gem

In *J. Am. Chem. Soc.*, **70**, 3509 (1948), the late Professor W. M. Latimer discussed an unusual preparation of the compound $C_6N_9H_3$, named *melon*. He mentioned that when exposed to air, the compound forms the monohydrate. One of my students suggested that the hydrate should be named *watermelon*.

William M. Spicer
Georgia Institute of Technology
Atlanta

James O. Osburn
University of Iowa
Iowa City

Analog computer instruction

A Plugboard Teaching Aid

The recent development of computers is creating fundamental changes in research and teaching. The use of computers creates new opportunities in all fields of science, including chemistry and chemical engineering. No chemistry teacher can afford to disregard the possibilities for using computers in his own teaching, nor of preparing his students to use computers in research and in industrial work.

Computers are classified according to operation as digital or analog. A digital computer can do a wider range of calculations, and has a higher precision than an analog computer. Nevertheless, the use of analog computers is increasing at a rapid rate (*1*).

The analog computer has several advantages (*10*):

Programs are relatively easy to set up.

It is particularly suited for the simulation of physical systems.

The program can include information, such as curves, which have not been reduced to mathematical form.

Parameter magnitudes can be changed easily to give a series of solutions for different parameter values. This is particularly valuable in preliminary curve-fitting.

It can be combined with non-computing elements, such as control systems.

For problems of moderate size, the analog computer is less expensive (*6*).

Teachers will find many opportunities to use analog computers for demonstrations in reaction kinetics, equipment design, and control. Some applications for which computers are well suited are (*4, 9, 12*):

Consecutive and simultaneous reactions
Catalytic Reactor design and operation
Distillation column dynamics
Control system simulation
Air pollution studies

A Typical Demonstration

Problems in chemical kinetics are often so complicated that a mathematical solution is hopelessly involved. Such problems can often be set up rather easily on a computer and the solutions demonstrated to a class. The following section illustrates how this would be done for the simple case of two consecutive first order reactions. This example includes a derivation of the basic concepts of analog computer programming. Those interested in pursuing the subject further should consult one of the excellent books on the subject (*2–5, 8*).

The equations for the consecutive first order, irreversible reactions

$$A \rightarrow B \rightarrow C \qquad (1)$$

are as follows:

$$x' = -ax \qquad (2)$$

$$y' = ax - by \qquad (3)$$

$$z' = by \qquad (4)$$

where x is the concentration of substance A, y is the concentration of substance B, z is the concentration of substance C, and the primes represent derivatives with respect to time.

The circuit for solving this problem is derived from the basic principles of analog computation.

Fundamental to the electronic analog computer is the high-gain dc amplifier, represented by the symbol shown in Figure 1. The gain, or ratio of output voltage to input voltage, is commonly between 20,000 and several million. If the output is not over 100 volts, therefore, the input will be less than 5 millivolts.

Figure 1. Symbol for amplifier.

This can be taken as essentially zero. The importance of this will become apparent in the circuit analysis which follows.

Resistors and capacitors are connected to the amplifier to form sub-units which perform addition, multiplication, or integration. The operation of these sub-units can be understood from an elementary consideration of the current flow in the sub-unit.

For addition and multiplication, a circuit is put together as shown in Figure 2.

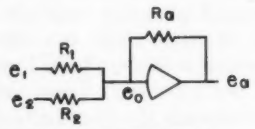


Figure 2. Circuit for addition and multiplication.

The current through a resistor is equal to the voltage drop divided by the resistance. Applying this law to Figure 2, we obtain

$$\text{through } R_1\text{, the current} = \frac{e_1 - e_0}{R_1}$$

$$\text{through } R_2\text{, the current} = \frac{e_2 - e_0}{R_2}$$

$$\text{through } R_a\text{, the current} = \frac{e_0 - e_a}{R_a}$$

No current goes through the amplifier, so the current through R_a is equal to the sum of the currents through R_1 and R_2, or

$$\frac{e_0 - e_a}{R_a} = \frac{e_1 - e_0}{R_1} + \frac{e_2 - e_0}{R_2}$$

Now since e_0 is essentially zero, we may write

$$-\frac{e_a}{R_a} = \frac{e_1}{R_1} + \frac{e_2}{R_2}$$

$$e_a = -\left[\frac{R_a}{R_1}e_1 + \frac{R_a}{R_2}e_2\right] \qquad (5)$$

For integration, the circuit is shown in Figure 3.

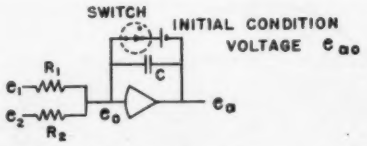


Figure 3. Circuit for addition and integration.

The current through a capacitor is given by the expression $C(dE/dt)$, where C is the capacitance, E the voltage across the capacitor.

Equating currents as before, we obtain

$$C\frac{d(e_0 - e_a)}{dt} = \frac{e_1 - e_0}{R_1} + \frac{e_2 - e_0}{R_2}$$

For $e_o = 0$,

$$-\frac{d(e_a)}{dt} = \left[\frac{e_1}{R_1C} + \frac{e_2}{R_2C}\right]$$

$$e_a - e_{ao} = -\left[\frac{1}{R_1C}\int_0^t e_1dt + \frac{1}{R_2C}\int_0^t e_2dt\right] \qquad (6)$$

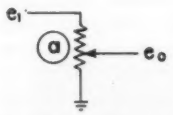


Figure 4. Potentiometer.

For multiplication by a positive number less than 1, a potentiometer is used as shown in Figure 4.

Applying these principles to the reaction problem, we start with equation (2):

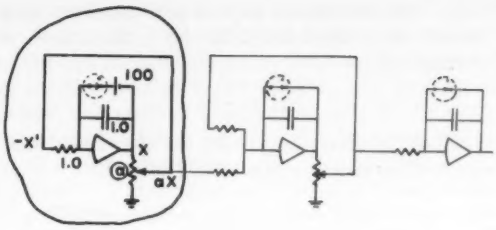
$$x' = -ax.$$

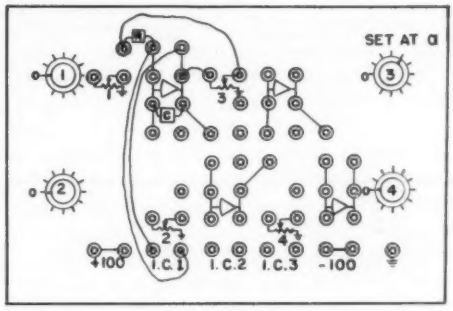
The output voltage of an integrating amplifier is arbitrarily assigned the value of the concentration x. The voltage at the input resistor, by equation (6), then represents $-x'$. (Note that an amplifier always gives a reversal of sign.) The integrating amplifier, as shown in Figure 5, is an amplifier with a capacitor in parallel and a resistor leading to the input. Leads also must be placed from "initial conditions" terminals to fix the value of x at zero time, when the computation begins. By equation (2),

$$-x' = +ax.$$

Assuming a to be less than 1, one obtains ax from x by using a potentiometer. The condition that $-x'$ be equal to ax is obtained by connecting the points representing these two quantities, as shown in Figure 5. This figure shows the wiring diagram in conventional symbols, together with a sketch of the wiring on a computer plugboard, which will be described in a subsequent section. Use of a 1 microfarad capacitor and 1 megohm resistor requires that time be expressed in seconds.

The circuit for y is designed in a similar fashion. Addition and integration are performed by the same amplifier. Let the output equal $-y$, whence the sum





R 1 MEGOHM RESISTOR

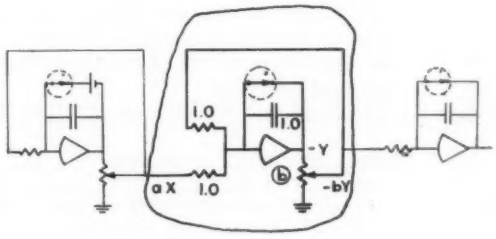
C 1 MICROFARAD CAPACITOR

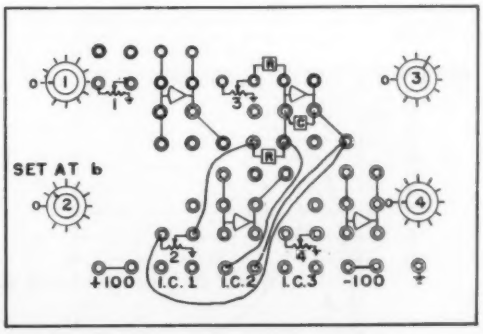
Figure 5. Circuit diagram and board wiring for $x' = ax$.

of the input terms is y'. By equation (3),

$$y' = ax - by.$$

A voltage representing ax is already available, and $-by$ is obtained from $-y$ by another potentiometer. These are added as shown in Figure 6, again using 1 megohm resistors and 1 mfd capacitors.





R 1 MEGOHM RESISTOR

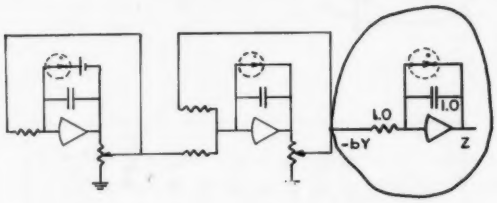
C 1 MICROFARAD CAPACITOR

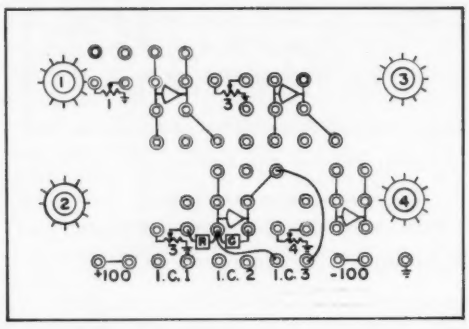
Figure 6. Circuit diagram and board wiring for $y' = ax - by$.

Finally, the simulation of z is performed by letting the output of a third amplifier be z, the input $-z'$, and noting that

$$-z' = -by.$$

The voltage representing $-by$ is already available. This part of the circuit is shown in Figure 7.





1 MEGOHM RESISTOR

1 MICROFARAD CAPACITOR

Figure 7. Circuit diagram and board wiring for $z' = by$.

The solution begins when the three switches which bypass the three amplifiers are opened simultaneously. The solution is in the form of three time-voltage curves, which are the analogues of the time-concentration curves in the physical situation.

Figure 8 shows the curves which were obtained on a Heathkit computer using the plugboard which is described in the next section. The initial conditions are 100 for x, zero for y and z; the values of the coefficients are $a = 0.4$, $b = 0.3$. The equations were also solved by calculus, and a few calculated points plotted to show the validity of the computer solution. The plugboard set up for solving this problem is shown in Figure 9.

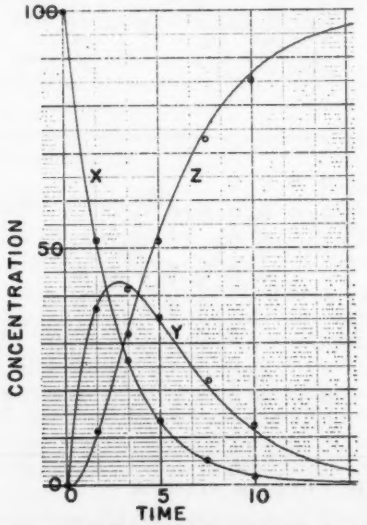


Figure 8. Computer solution for simultaneous first order reactions. ——Computer, O Calculated.

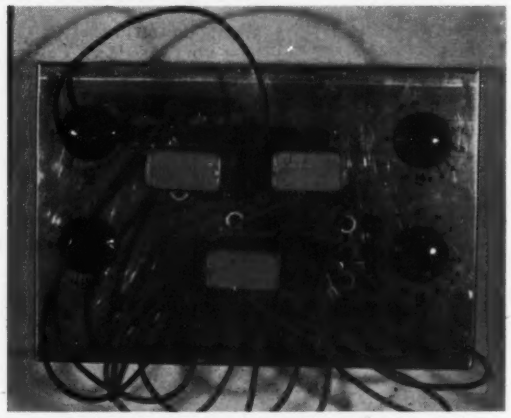


Figure 9. Plugboard programmed for solution of kinetics problem.

The computer can be useful even for this simple example in showing the effects of changing coefficients and initial conditions. These can be changed by resetting potentiometers to different values, and new solutions obtained very easily. The computer can also be used for reversible reactions, reactions of higher order (*11*), several reactions in series and competing reactions where a mathematical analysis would be impractical.

The Auxiliary Plugboard

After watching a demonstration on a computer, many students will want to learn how to operate the computer themselves. In view of the growing use of computers in industry, the student can profit by learning how to use a computer while in school. Many feel that this is a proper part of the undergraduate curriculum in chemistry and chemical engineering (*7*).

For teaching computer use, laboratory instruction and practice is very desirable. Although a high precision computer is beyond the budgets of many college departments, a less expensive model is quite satisfactory for instruction. These computers of lower accuracy are quite suitable for teaching computer programming and operation. Computers can be obtained for as little as $200 in kit form, and several companies offer small computers for less than $5000. For information about available computers, the reader is referred to a recent list compiled by Williams (*9*). A satisfactory recorder will cost about $500. Thus, investment in a computer should offer no serious problem.

However, even with an inexpensive computer, the instructional cost per pupil is apt to be excessive. Space at the computer is limited, and a student tends to use a lot of time in setting up a problem. This sets a severe limit to the size of a class, and the instructor's time is taken by a very few students.

One solution has been to give lectures on computer operation, then let each student reserve time on the

computer and work out his problems by himself. This has not worked well, as students usually need some help and supervision.

We have found that the use of auxiliary plugboards has provided a very satisfactory solution to the problem of student use.

Essentially, the auxiliary plugboard consists of a number of terminal jacks arranged to resemble a section of the computer plugboard. When the board is plugged into the computer, the jacks are connected in parallel to similar jacks on the main plugboard. The board shown in Figure 10 was developed for use with a Heathkit computer; it could easily be adapted to other computers. A commercial model has been introduced by the Donner Co. for use with their Model 3500 computer.

The base of the auxiliary board shown in Figure 10 is a 3 × 8 × 12 in. aluminum chassis. Colored jacks for four operational amplifiers are arranged in imitation of the Heathkit board. In addition, plugs for reference voltages, ground potential, and three sets of initial conditions are included. Each jack or set of jacks is wired to an 18-connector outlet. The plug which mates with this outlet makes connection with the corresponding jacks on the main plugboard. "Initial conditions" terminals are wired to initial conditions voltage sources through relay switches. Four 100 K ohm carbon potentiometers are wired as shown on the schematic painted on the board; one side of a potentiometer is connected to ground, the other side and the center tap connected to plugs which are located near the amplifier plugs. The potentiometers were calibrated in place.

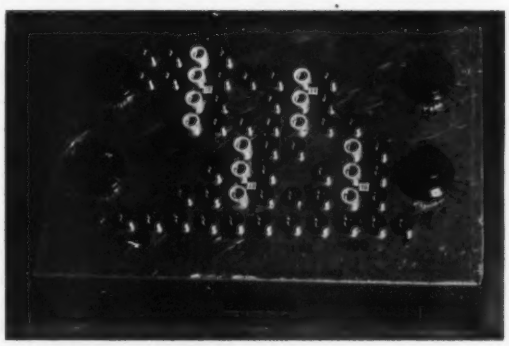


Figure 10. Auxiliary plugboard.

In the computer laboratory, each student gets an auxiliary board and a supply of capacitors, resistors, and connectors. Each capacitor or resistor is attached to a General Radio double jack, which can be inserted into the appropriate plugs on the board. After a lecture on the principles involved in the solution of a problem, the student proceeds to set up the program on his board. When he is ready, he plugs the board into the main computer with the assistance of the instructor. The solution is recorded in a short time.

For some problems, the solution is a voltage read on a voltmeter. For problems in which there are differential equations, the solution is a voltage *vs.* time trace recorded by a recording voltmeter, or a trace appearing on the face of an oscilloscope.

By using the inexpensive plugboards, several students can be working on their programs at the same time, with the help of only one instructor. Each student uses the main computer only a relatively short time.

More complicated problems, such as second order equations, require function multipliers or function generators. Commercial units are fairly expensive, but units which have enough accuracy for student laboratory use can be assembled for a small fraction of the cost of a commercial unit, and will serve for instructional purposes. (The author will gladly answer requests for information as to details of such units and of the construction of plugboards.)

Acknowledgment

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NSF Supports Teaching Equipment Development in 1962

NSF will continue to support the teaching equipment program inaugurated in 1959. Proposals are now being sought for 1962. Proposals for support under the Science Teaching Equipment Development Program should be sent not later than November 15, 1961, to the Course Content Improvement Section, National Science Foundation, Washington 25, D. C. Fifteen copies of a proposal are required. Awards will be announced in March 1962.

Bernard Siegel
Aerospace Corporation
El Segundo, California

Hydride Formation by Atomic Hydrogen Reactions

Statements can be found in the literature to the effect that almost all metals react with atomic hydrogen to form hydrides (*23*, *34*). However, review articles on atomic hydrogen reactions generally have emphasized the action of atomic hydrogen on organic compounds and simple inorganic gases (*21*, *26*, *64*, *72*). Little attention was given in these reviews to hydride formation by the action of atomic hydrogen on metals or metal-containing compounds. For this reason it was felt that a thorough analysis of the role of atomic hydrogen in hydride formation was necessary.[1] The discovery in recent years of new hydrides of many metals, particularly the less stable hydrides, makes possible at this time a more critical examination of atomic syntheses reported in the older literature. Many of these claims now appear unlikely in view of presently known properties of hydrides. A significant point found by searching through the literature on atomic hydrogen syntheses is that the abstracts of these papers are often in error. An example of this are claims in abstracts for the formation of hydrides that are not described in the original papers; this was particularly prevalent for papers published during the 1920's and 1930's.

Confusion also exists in the naming and indexing of atomic hydrogen reactions. In the present paper hydrogen atoms are assumed to be the active species when the experiments were carried out as follows:

(I) Atomic hydrogen was generated in a separate chamber and transported down a tube, whose wall was suitably poisoned for hydrogen atom recombination, to intersect with a second gas stream or impinge on a target surface.[2]

(II) Reactions in a single chamber when hydrogen was dissociated at a hot filament and the second species was either a non-volatile target or in an uncombined state.

(III) Reactions in a single chamber when hydrogen was dissociated by inelastic collisions with photo-excited mercury atoms and the second reactant did not react in this manner.

For these cases the origin of the atomic hydrogen was not specified. Reactions of mixtures of gases in a discharge tube might well involve gaseous ions or radicals from the other reactant and are not considered here. However, when hydrogen is the only volatile species in a discharge, and the hydrogen thus activated is subsequently reacted with a non-volatile target present in the discharge chamber, it is certainly possible that the attacking species is atomic hydrogen (*64*). For such cases the origin of the active species is specified in the paper, whether in a low pressure electric discharge or a higher pressure silent discharge.

Hydrides of Main Group Elements

I-A Elements

These metals all form solid univalent ionic hydrides when heated in hydrogen (*34*); this reaction does not occur at ambient temperatures, even for thin films of the metal (*19*). Although specific compositions have not been proved, strong chemical evidence exists that atomic hydrogen reacts with these metals to form ionic hydrides.

The formation of a surface layer, assumed to be a hydride, was reported when sodium metal was reacted with hydrogen activated in an electrodeless discharge (*68*). A similar observation, backed by chemical proof of hydride hydrogen, was reported when a sodium-potassium alloy was reacted with atomic hydrogen (*48*). Mirrors of lithium, sodium, and potassium reacted separately with atomic hydrogen to form hydridic compounds; the entire deposit could be reacted if underlying layers of thicker mirrors were driven thermally to the surface in a step-wise process (*19*). However the weak point in these experiments was the lack of temperature control over the metal surface. While it was claimed that these were ambient temperature experiments, it can be reasonably assumed that atomic hydrogen recombinations raised the target temperatures to elevated temperatures. Therefore while ionic hydrides apparently form in these reactions, the assertion that the reactions proceed at ambient temperatures is not proved; it may be that these reactions proceed at temperatures not very much below those at which molecular hydrogen reacts.

II-A Elements

Beryllium and magnesium form polymeric $(BeH_2)_x$ and $(MgH_2)_x$ solids which are believed to be bonded by hydrogen bridges, rather than the ionic hydrides formed by heavier II-A metals. The more stable magnesium hydride can be formed from magnesium and hydrogen at 570° and 200 atmospheres (*79*), but $(BeH_2)_x$ decomposes rapidly at 125° and atmospheric pressure and cannot be formed by the action of hydrogen on the metal. Beryllium has been reported to react with atomic hydrogen to form a surface film after seven hours under conditions in which the target surface had

[1] For the purpose of this paper, all binary compounds of hydrogen are considered to be hydrides.

[2] Details of the methods used to generate atomic hydrogen can be found in the reviews cited above and in the papers of the text. The act of dissociation has been achieved by thermal dissociation at a hot filament, condensed and non-condensed electric discharges, and electrodeless discharges.

to exceed 150° and often exceeded 170° (*58*). In view of the instability of beryllium hydride at these temperatures and the scanty evidence presented, it must be doubted that beryllium hydride has yet been made by an atomic hydrogen reaction.

Of the heavier II-A metals the only observation recorded was film formation when calcium was reacted with hydrogen activated in an electrodeless discharge (*68*). However these metals should react with atomic hydrogen to form hydrides since the corresponding reaction occurs at elevated temperatures with molecular hydrogen at atmospheric pressure for all except magnesium.

III-A Elements

The action of atomic hydrogen on boron or on any of the known boron hydrides has not been reported. The role of atomic hydrogen in interconversion reactions of the boron hydrides should prove extremely interesting. Diborane condenses rapidly at temperatures greater than 100° into various members of the volatile borane series (*49*) while the highest of the known boranes, decaborane, condenses rapidly into polymeric $(BH)_x$ at temperatures exceeding 200° (*71*). An indication of the synthetic possibilities of atomic hydrogen on boron can be inferred from recent work with molecular hydrogen. It was found that the latter reacted with boron heated to 840° to form diborane (apparently only traces) when passed rapidly over the heated metal (*47*).

Aluminum. The only known hydride of aluminum is a polymer, $(AlH_3)_x$. That aluminum does not form a series of volatile hydrides similar to the boranes can be attributed to its greater coordination number and the resultant instability of the simple electron-deficient dimer. The polymer is not sufficiently stable to enable formation directly from the metal and hydrogen. Repeated attempts in several laboratories known to the writer have failed to yield aluminum hydride by such a synthesis at extremes of both temperature and pressure.

However, a recent study of the action of atomic hydrogen on aluminum has resulted in the formation of a hydride which is stable below 0° (*70*). This hydride was formed by the action of atomic hydrogen on aluminum evaporating to a surface at −195°; evidence was presented for a heterogeneous reaction at the cold surface. The proof for hydride formation was kinetic in character with the product represented as AlH_x where x is greater than unity. The uncertainty in the hydride content was attributed to decomposition of initially formed hydride molecules by the destructive action of atomic hydrogen recombinations. Because of its lesser stability the hydride formed in this manner is obviously different from $(AlH_3)_x$.

Gallium, Indium and Thallium. The stabilities of the known hydrides of these metals decrease with increasing atomic weight of the metal. $(GaH_3)_x$, unstable above 140° (*85*), $(InH_3)_x$, unstable above 80° (*84*), and $(TlH_3)_x$, unstable at ambient temperature (*78*) are the known trivalent hydrides of these metals. $(TlH_3)_x$ decomposes at ambient temperature to $(TlH)_x$ which is stable to 270° (*78*), but this reaction has not been reported for Ga, In, or Al hydrides. The lone volatile hydride reported for these metals is digallane (*81*) but the reported high stability of this compound and the absence of such a dimer in aluminum hydride and indium hydride chemistry make the existence of such a volatile hydride extremely improbable. Although the heavier III-A metals do not react with hydrogen, evidence has been obtained by Pietsch and his co-workers for hydride formation when these metals were reacted with atomic hydrogen (*56*, *57*).

Gallium was reported to react with atomic hydrogen at target temperatures approaching 170° to form a hydride film after 15 hours (*58*). The composition of this hydride was not determined, but tests for hydridic hydrogen were presented. However unless the temperature measurement was in error, the prolonged exposure of the product to temperatures approaching 170° is in conflict with the stability data on $(GaH_3)_x$. In the same investigation, indium vapor was reported to react with atomic hydrogen at 120–130° to form a condensable hydride which formed an indium mirror on warming, while molten indium was claimed to form a hydride on the surface of the metal. These observations are also in conflict with the stability data on $(InH_3)_x$. One must conclude that atomic hydrogen reactions did not lead to the known trivalent hydrides of these metals and it is doubtful if true hydride formation has been proved for these reactions.

Thallium(I) chloride was reported to react with atomic hydrogen to form a condensable product (*56*). Evidence presented was the formation of a metal deposit at a distance of 4 cm from the TlCl charge; in view of the extremely low vapor pressure of TlCl and Tl at the temperature of the chloride surface (217°) volatile hydride formation was assumed. A similar experiment with thallium metal at 136.5° gave the same result (*58*). The evidence presented in light of the known stability patterns of $(TlH_3)_x$ and $(TlH)_x$ indicate that neither of these hydrides was formed. It is likely that a hydride radical which decomposed to the metal on condensation was the actual product; less probable would be a volatile TlH_3 species which decomposed on condensation rather than condense to a stable polymeric form. It is very unlikely that the wall temperature could have exceeded the decomposition temperature of $(TlH)_x$.

IV-A Elements

Carbon. While the reaction of carbon and hydrogen to form methane requires temperatures over 500° (*34*), the corresponding reaction with atomic hydrogen proceeds at ordinary temperatures. Günthersehulze found that the wall of a hydrogen discharge tube was covered with carbon when a small charge of the latter was placed in the tube (*27*); under the conditions of the experiment it was argued that a volatile hydride intermediate was required to explain this migration. Subsequent investigators have definitely shown that methane is formed when atomic hydrogen reacts with thin deposits of soot, at temperatures to 100° (*3*, *7*, *28*). Harris and Tickner also found traces of C_2–C_5 hydrocarbons as products.

Silicon and Germanium. Both of these elements form paraffin compounds which are less stable than the analogous hydrocarbons; for this reason germane and silane have not been synthesized by the action of hydrogen on

the metal. The hydrides Ge_4H_{10} and Ge_5H_{12} have recently been prepared (*2*). While the latter are only stable to 50°, disproportionation results in the formation of a polygermane $(GeH_2)_x$ which is stable to 350°, the same as for GeH_4; thermally stable $(SiH)_x$ is also known (*65*, *66*). In view of these stability data it would be surprising if silicon and germanium did not react with atomic hydrogen to form both series of hydrides.

Yet there is almost nothing in the literature on the reaction of silicon with atomic hydrogen, except perhaps for an early observation that traces of a condensable compound were trapped after a discharge through hydrogen in a glass apparatus (H-SiO_2 reaction), with the product exhibiting a silane-like odor (*33*). Various claims for the formation of a volatile germanium hydride by atomic hydrogen reactions have been made but no definite hydride has been proved (*25*, *52*, *53*). Pearson trapped a volatile substance at −195° and showed that hydrogen could be subsequently driven from this "hydride" by warming but no composition was given and proof of true hydride formation was not demonstrated. Glemser noted that the reaction between GeO_2 and atomic hydrogen led to the formation of a germanium mirror on the reactor wall, claiming intermediate hydride formation; obviously this hydride was not GeH_4 or any of the higher germanes since the latter disproportionate to $(GeH_2)_x$ which is stable to 350°. In this case the formation of a radical hydride that decomposed to the metal on condensation is indicated.

Tin and Lead. Volatile SnH_4 and PbH_4 are known, and quite recently a Sn_2H_6 has been reported (*35*); these hydrides are all unstable at ambient temperatures. Polymeric stannanes or plumbanes are not known. Stannane has been proved as a product of atomic hydrogen reactions but only indirect evidence exists for lead hydride formation by such reactions.

Inconclusive evidence for tin hydride formation was advanced by the action of atomic hydrogen on tin (*53*) and in a discharge through hydrogen with tin electrodes (*20*). However, Paneth identified SnH_4 as a product of the reaction between tin and hydrogen activated in a discharge (*52*), and Vdovenko proved SnH_4 results from atomic hydrogen attack on $SnCl_4$ (*76*), and $SnCl_2$ (*77*); the charges of tin chloride were maintained at very low temperatures, below the decomposition point of stannane. The very low yields in these studies were attributed to the fact that only 0.3% of the atomic hydrogen collisions with chloride surface were successful.

Volatile, condensable, but otherwise unidentified hydride products from the action of atomic hydrogen on lead (or in discharge tubes) have been reported by several investigators (*20*, *51*, *56*). Schultze and Müller in similar experiments found that the trapped "hydride" could not be re-evaporated (*67*). This could be attributed to the formation of PbH_4 and its subsequent decomposition on warming, in view of the instability of PbH_4 at ambient temperatures. It was also found that lead chloride reacted with atomic hydrogen to form a lead deposit on the wall of the reactor (*56*); this might also be attributed to the instability of lead hydride. However the possibility that the hydride which was formed was in fact a hydride radical rather than PbH_4 cannot be precluded.

V-A Elements

Nitrogen. Because of the stability of the triple bond in nitrogen, a reaction between atomic hydrogen and nitrogen is not achieved readily and only traces of ammonia have been observed at 357° (*50*). Hydrazine has not been found in this reaction and moreover the latter is readily decomposed by atomic hydrogen to the more stable ammonia (*16*); the rate of reaction between atomic hydrogen and ammonia is very slight (*8*, *15*, *16*, *30*). The reaction between atomic hydrogen and nitrogen atoms to form ammonia occurs readily (*73*). Ammonia also results from the action of atomic hydrogen on many inorganic salts containing nitrogen; such salts include nitrides, cyanides, nitrates, nitrites, amides, and isothiocyanates (*38*). The action of hydrogen activated in a silent discharge converts many ammonium salts to ammonia (*41*, *42*, *45*).

Phosphorus. Because there is no triple bond in phosphorus, the latter reacts with atomic hydrogen much more readily than does nitrogen; the synthesis of phosphine by this reaction has been frequently reported (*9*, *38*, *40*, *86*). Traces of the less stable diphosphine have also been found from this reaction (*86*). It has been claimed that atomic hydrogen reacts with phosphine to form a mirror which was assumed to be a lower hydride of phosphorus (*15*). However it has also been reported that red phosphorus and hydrogen are the sole products of this reaction (*86*). In any case, phosphine is more susceptible to hydrogen atom attack than is ammonia and the proved existence of higher phosphines and polymeric hydrides indicates that the study of the role of atomic hydrogen in these conversions should be valuable. Higher phosphines, such as P_3H_5, have recently been reported to result from the disproportionation of diphosphine, although the evidence was by Raman Spectra and indirect analysis (*6*). A polymeric $(P_2H)_x$ was early reported (*74*) but subsequently disputed on the basis of adsorbates of phosphine on phosphorus (*60*). However the existence of such a polymer has recently been proved from the decomposition of diphosphine (*18*), and $(PH)_x$ has also been recently reported (*83*).

Futile attempts have been made to synthesize a pentavalent hydride of phosphorus, both by atomic hydrogen reactions (*15*) and very low temperature synthetic methods (*82*). It can be shown, however, that such a hydride is theoretically impossible as a result of the diffuse nature of the *d*-orbitals of phosphorus in the ground state (*12*). Bond formation in such cases requires extremely electronegative ligands, such as fluorine (*13*).

Arsenic. The reaction between atomic hydrogen and arsenic has often been reported to result in the formation of a volatile hydride (*9*, *27*, *52*, *53*, *69*) and this was also found for the action of hydrogen activated in a silent discharge on arsenic pentoxide (*41*). Although the specific hydride was not proved, it is probable that arsine was formed since it is stable to 300°. A diarsine was prepared recently but this hydride decomposes above −100° into arsine and a polymer, $(As_2H_{1.2-1.3})_x$, stable to 350° (*46*); the polymer is probably $(As_2H)_x$ and has been reported elsewhere (*36*). There was no indication of such polymer formation in the reported atomic hydrogen reactions.

Antimony and Bismuth. The only known hydrides of these elements are SbH_3 which decomposes slowly at ambient temperatures, and BiH_3 which is quite unstable at these temperatures (*34*). Claims have been made that atomic hydrogen reacts with these metals to form hydrides but these are better established for antimony than for bismuth.

The formation of a metal mirror was reported when atomic hydrogen was reacted with Sb_2O_3 (*38*); similar mirrors formed when hydrogen activated in a silent discharge was reacted with $SbCl_3$, Sb_2S_3, and Sb_2O_5 (*41*). A condensable hydride from which hydrogen could subsequently be driven by warming was also reported (*53*), although true hydride formation was unproved. Bagdasaryan and Semenchenko reported that a hydride, presumably SbH_3, results from the H-Sb reaction, and calculated that only one collision in 90 was effective (*4*).

Early investigators claimed that atomic hydrogen reacts with bismuth to form an unstable volatile hydride, without real proof (*20, 27, 52*); this was disputed by Pearson (*53*). A more recent study by Harris and Tickner, in which they found that a bismuth mirror appeared to travel a distance of 25 cm, lends credence to the intermediate hydride theory (*29*); an average life of 0.4 seconds was calculated for the unstable hydride. Kroepelin also found that atomic hydrogen reacts with bismuth nitride to deposit a bismuth mirror at a large distance from the source (*38*). In view of the instability of BiH_3 under the experimental conditions of these studies, it is not possible to choose between the latter and a hydride radical as the probable reaction product that was observed.

VI-A Elements

Oxygen. Geib has reviewed the extensive literature on the reaction between hydrogen atoms and oxygen to 1936 (*21*) and a detailed review by Rodebush (*59*) was published shortly thereafter. Considerable effort has been expended in recent years on the mechanism of this reaction and related reactions, but it would not be appropriate to review this extensive literature here. In summary however, it can be stated that atomic hydrogen reacts with oxygen to form H_2O_2 at $-195°$, and to form water at ambient temperatures. Further, hydrogen atoms decompose H_2O_2 at ambient temperatures to form water and do not react appreciably with water itself. It has been claimed that atomic hydrogen reacts with ozone at $-195°$ to form the superoxide H_2O_4, which decomposes on warming to H_2O_2, H_2O, and O_2 (*37*). However Giguere and Chin have disputed this since they found by infrared spectroscopy that only the latter products were formed (*24*).

Sulfur. Like oxygen, sulfur reacts readily with atomic hydrogen at ambient temperatures to form the analogous hydride, H_2S; there is no report of polysulfide formation by atomic hydrogen reactions (*5, 9, 38, 41, 48, 68, 69*). Hydrogen sulfide can be prepared also by the action of atomic hydrogen on solid salts such as sulfates and isothiocyanates (*38*); sulfides (*41*), thiosulfates (*43, 44*) and sulfites (*43, 44*) also yield H_2S when these salts are reacted with hydrogen activated in a silent discharge. The hydride has even been prepared by bubbling atomic hydrogen (diluted with inert gas) through thiosulfate (*31, 32*) and sulfuric acid solutions (*14*).

Efforts to form a higher hydride of sulfur by reaction of H_2S with atomic hydrogen resulted only in the decomposition of the hydride to sulfur and hydrogen (*15*). These efforts should prove futile for reasons identical to those advanced for phosphorus.

Selenium and Tellurium. Unlike the lighter VI-A hydrides, tellurium hydride is too unstable to be prepared directly from the elements (*34*). Inconclusive claims of the formation of both H_2Se and H_2Te by the action of atomic hydrogen on the elements have been advanced (*27, 29, 52, 53*) and mirror evidence has been reported for the action of hydrogen activated in a silent discharge on targets of selenious and tellurous acids (44). Bagdasaryan and Semenchenko have presented the most convincing evidence (*5*); only one tenth of the atomic hydrogen collisions with the elements were calculated to be successful.

VII-A Elements

Atomic hydrogen converts each of the halides to the corresponding hydrogen halide; the gas phase reactions are covered in the reviews cited above. The hydrogen halides can also be formed by the action of hydrogen activated in a silent discharge on solid halides (*41, 43*). Atomic hydrogen reacts also with aqueous iodine solutions to form HI (*38*).

Hydrides of Transition Elements

I-B Elements

Copper, silver, and gold have exhibited evidence for transient volatile hydride species, but the only definitely known hydride is solid CuH which decomposes above 60° (*34*). The reaction of these metals with atomic hydrogen have been investigated by Pietsch and his co-workers (*54, 56, 58*).

Copper was described as forming a film after 30 minutes of exposure to atomic hydrogen, with some evidence presented for hydridic hydrogen. Although no temperature was given it is likely that the target surface greatly exceeded the reported decomposition temperature of CuH. Silver was described as forming good yields of a stable hydride powder with a target temperature of 250–350°; decomposition of the hydride was reported to commence only at temperatures approaching 600°. On the other hand X-ray diffraction patterns of the hydride were identical to those of silver, and the unusual thermal stability reported for the hydride is not believable. Gold foil formed a film after one hour, with some evidence advanced for hydridic hydrogen. However, the heaviest metal hydride in a group of the periodic table generally exhibits the least stability, and the temperature of the gold target should have exceeded the decomposition temperature of any conceivable gold hydride. It must therefore be doubted that hydride formation has been proved for atomic hydrogen reactions with the I-B metals.

II-B Elements

Definite divalent hydrides have been found for zinc and cadmium and evidence for the existence of a less stable mercury hydride has been obtained (*80*); ZnH_2 is stable to 90°, CdH_2 to $-20°$, and HgH_2 to $-125°$. Of these metals, only mercury has been studied in atomic hydrogen reactions.

Spectroscopic evidence for hydride formation was found when mercury reacted with atomic hydrogen (*10*). Geib and Harteck reported that a hydride was formed when mercury vapor at 100° was mixed with atomic hydrogen in a vessel whose wall was maintained at −195°. Under comparable conditions molecular hydrogen did not react. The hydride formed by the hydrogen atom reaction decomposed at temperatures above −125° (*22*). While no justification for neglecting physical adsorption was presented, especially in view of the low temperature at which the bound hydrogen was released, it is interesting that the reported decomposition temperature coincides with that reported for the hydride prepared by synthetic methods. In a more recent investigation it was found that a discharge through hydrogen and mercury resulted in the formation of a "hydride" which decomposed above 150° (*17*). However, this observation is in complete conflict with the reported stabilities of the known II-B metals.

Other Transition Elements

The only other metal whose positive reaction with atomic hydrogen has been reported is tantalum. Pietsch and Lehl (*55*) found that finely ground tantalum reacted with atomic hydrogen to form a hydride; they observed the reaction by X-ray diffraction techniques. It was further found that repulverization of the target, followed by further atomic hydrogen treatment, completely converted the sample. However the composition of the hydride was not determined. Although the hydride formed by the treatment of tantalum with molecular hydrogen at elevated temperature generally has a H/Ta ratio less than one (*11, 34*), TaH, TaH_2, and TaH_3 have recently been reported by a Grignard synthesis (*39*). The other V-B metals present an equally confusing pattern. Vanadium has not been reported to form a hydride with hydrogen content greater than $VH_{0.94}$ (*75*). Yet NbH_2, which is stable to 300° (*1, 11*) has been reported although it was previously believed that NbH was a limiting composition.

Another intriguing situation can be found in the group VIII metals, which generally form "hydrides" of low hydrogen content on heating the metal in hydrogen. However a recent series of papers by Sarry (*61, 62, 63*) presents evidence for the formation of FeH_2, FeH_3, CoH_2, and NiH_2 by Grignard reactions, although specific hydrides were not isolated and complex stabilization was inferred.

Conclusions

In summary it may be stated that hydride formation by atomic hydrogen reactions has not been proved for many metals. In cases where the metal reacts with molecular hydrogen to form a thermally stable ionic hydride or covalent hydride, the analogous reaction with atomic hydrogen generally proceeds at a lower temperature. This is not surprising since the energy barrier required to dissociate hydrogen has already been surmounted. However, for the many metals which form covalent hydrides that are not stable to high temperatures, the pattern is unclear. In such cases the reported claims of atomic syntheses are often in complete conflict with presently known stability behavior of the corresponding hydrides. The inference here is plainly that the claims are unfounded. Many such metals form a series of hydrides by synthetic methods, but the role of atomic hydrogen in these interconversions is generally unknown since the techniques used were often insensitive to all but the stablest of the hydrides. For metals which form hydrides which are unstable at ambient temperatures, it is not possible to decide whether the observed indirect evidence for hydride formation by atomic hydrogen reactions is the result of true hydride formation or hydride free radicals.

While the evidence is sufficient to state that the main group elements probably would all form hydrides (either complete molecules or free radicals) by atomic hydrogen reactions carried out under appropriate experimental conditions, this is not true for the transition elements. The metals in groups VI-B, VII-B, and VIII form loose types of hydrides when reacted with hydrogen at elevated temperatures that do not necessarily involve covalent metal-hydrogen bonds; evidence to the contrary has not been definitive. Many of these metals fail to form a mirror by hydrogen atom attack under conditions that result in mirror formation by main group elements. Thus even hydride radicals are unknown for many metals.

The areas of uncertainty described above might profitably be investigated by atomic hydrogen reactions if the limitations of the past studies were circumvented. Definitive experiments with hydrides that are thermally unstable should not be carried out on solid targets that are heated by unavoidable atomic hydrogen recombinations. This also applies to the disruptive effect of atom recombinations on the product surface even if maintained at low temperatures. The best approach appears to be the use of physico-chemical techniques that minimize surface effects or eliminate them. Molecular beam techniques and time of flight mass spectrometry come to mind as possible alternatives.

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Report on Biophysics Institute Available

Since its creation in 1955 the Biophysics and Biophysical Chemistry Study Section of the NIH, in addition to its customary function of reviewing research grant applications, has been conducting special programs of activities to stimulate the development of biophysical research and training. In this connection the Study Section organized and sponsored an experimental conference, the Summer Institute in Biophysical Science.

The Summer Institute was held in Cambridge, Mass., from August 28 to September 9, 1960, and was attended by 63 students from 16 outstanding small liberal arts colleges. The Institute was designed to demonstrate the ways in which the principles of the physical sciences are applied to the investigation of biological problems, and to answer the questions "What is biophysics?" and "Why biophysics?" By exposing students to current biophysical research it was anticipated that some would undertake graduate studies in this field.

The central theme of the program was molecular biology; however, sessions on organ systems and instrumentation were also included. Throughout, emphasis was placed on the biological aspects of subjects discussed.

The report on the organization and evaluation of the Summer Institute is available from Dr. Walter L. Koltun, Principal Consultant, Biophysics and Biophysical Chemistry Study Section, 2020 Milvia Street, Room 300, Berkeley 4, California. The supply is limited.

George C. Brumlik
New York University
New York

Molecular Models Featuring Molecular Orbitals

According to the modern theories of valence, atomic and molecular orbitals have characteristic shapes and spatial orientation. The directional properties of the orbitals which are traced by valence electrons determine the structure of molecules and play an important role in chemical reactions. However, the currently available molecular models do not portray these orbitals by their construction.

To fill this gap, molecular models have been constructed which attempt to represent atomic and molecular orbitals as accurately as the current theories of valence and pertinent experimental evidence permit. This molecular model set is simple, consisting of a small number of basic units, and yet can be used to build models of a large variety of molecules, ions, and chemical intermediates. The model of a molecule is constructed so that first the models of atoms are assembled in the hybrid form required and then these atomic models are connected to form the model of the molecule.

The Molecular Orbital Models (as they shall hereafter be referred to) are based upon valence bond theory, which accounts for the shape and directional character of covalent bonds, and molecular orbital theory, which stresses the concept that polynuclear orbitals belong to the molecule as a whole. The atomic and molecular orbitals are shaped in accordance with the published v.b. and m.o. theoretical calculations (*1*, *2*, *3*) and their dimensions on the relative scale conform to van der Waals radii obtained from X-ray diffraction (*4*).

In the construction of Molecular Orbital Models of specific molecules, the principle of Gillespie and Nyholm (*5*) can be profitably employed. This principle is based upon the observation that the pairs of electrons in a valency shell—irrespective of whether they are shared (bonding) pairs or unshared (non-bonding) pairs—are arranged in a definite pattern which depends only on their number. This principle appears to hold for the non-transitional elements. Its use greatly facilitates the decision as to which is the most reasonable hybrid state of a particular atom-member of a molecule.

Based in part on a paper read before the Division of Chemical Education at the 137th Meeting of the ACS, Cleveland, April 1960.

The author is indebted to New York University for an Arts and Science Research Fund grant which made this work possible.

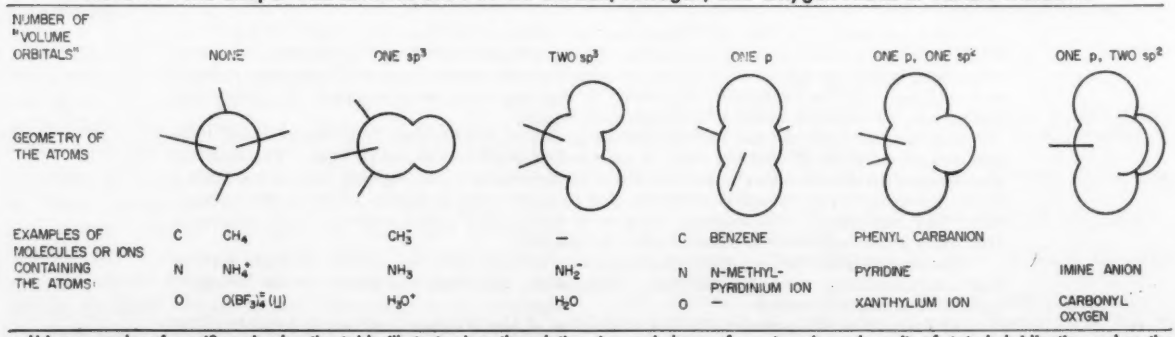
Geometry of Atoms and of Atomic Orbitals

A fully saturated atom (an atom all of whose valence electrons are used in sigma bonds) approximates a sphere defined by its covalent radius. If the atom is not fully saturated, electronic lobes extend in definite geometric patterns beyond this covalent core of the atom. These lobes are traced by unshared electron pairs, a lone electron, or by electrons which form polynuclear pi orbitals. The sigma bond orbitals, located mainly between the atoms which they unite, do not contribute to the molecular volume aside from their effect upon the size of the covalent core of the atom.

An atom can take a number of geometrical forms, and its volume can vary greatly, depending upon the molecule of which it is a part. Both the shape and the size of an atom depend on the state of its hybridization and also upon the number of unshared electron pair orbitals that it carries. The orbitals which contribute to the atomic volume over and above the volume of the saturated atomic core are here termed "volume orbitals."

Table 1 shows with specific examples the shapes and sizes which can be assumed by atoms of carbon, nitrogen and oxygen in the sp^3 and sp^2 states of hybridization in the proper relative proportions to the saturated covalent core of the parent atom. It can be seen that as the number of p orbitals and unshared electron pair orbitals becomes larger, the volume of the atom increases and its shape becomes more complex.

Table 1. The Shapes and Relative Sizes of the Carbon, Nitrogen, and Oxygen Atoms in Various Molecules



Using examples of specific molecules, the table illustrates how the relative size and shape of an atom depends on its of state hybridization and on the number of unshared electron pair orbitals.

The Design of the Molecular Orbital Models

A set of molecular models should meet two basic requirements: it should be able to represent the largest variety of molecules in the greatest possible detail and it should have only a few simple components. The atom in the Molecular Orbital Model set has been designed to be assembled from the two basic parts, the covalent saturated atom core and the orbital caps. The latter represent unshared electron pair orbitals and also serve as components of polynuclear π orbitals. Since the covalent radius of a particular atom in a given state of hybridization does not vary appreciably from molecule to molecule, the covalent cores of atoms are rigid to compression, yet flexible enough to permit angle bending. On the other hand, the hydrogen atoms and the orbital caps representing the volume orbitals are resilient in order to reflect the compressibility of van der Waals radii. The bodies are made of Adiprene L-100[1] on the scale 1 Å to 0.5 in.

The components of the Molecular Orbital Model set are shown in Figure 1. The covalent atomic cores with short fasteners inserted into undersized holes are on the bottom row. The bodies in the upper corners are used in the representation of unshared electron pair and molecular pi orbitals. Two additional fasteners are included: one a modified thumbtack, the other a stick whose length can be adjusted.

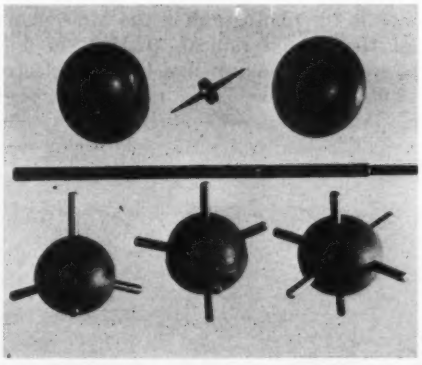


Figure 1. Components of the Molecular Orbital Models. Bottom row: covalent atomic cores with removable fasteners (left to right) tetrahedron, trigonal bipyramid, octahedron. Top row (left to right): one of the two *p* orbital lobes, a modified thumbtack fastener, a lobe representing hybrid unshared electron pair orbitals. Middle: adjustable stick fastener.

The indentation in the *p* orbital cap (Fig. 1, upper left corner) permits the representation of overlap of atomic *p* orbitals to form molecular pi orbital systems.

The sp^3, sp^2, and *sp* orbitals have two lobes of unequal size (*1*). Since the smaller lobe is within the general space of the covalent core region, only that part of the above mentioned hybrid orbitals that corresponds to the larger lobe is made visible in the models (Fig. 1, upper right corner).

The covalent atomic cores bear holes for fasteners that are used either to attach the orbital lobes or to connect the atomic cores together. The joining of the atomic cores represents the formation of a sigma bond. In agreement with theory, the pi bond is formed in the models by the parallel overlap of *p* orbital lobes.

[1] Adiprene L-100, a brand product of E. I. du Pont de Nemours & Co., Inc.

The fasteners on the covalent atomic cores are arranged in specific geometric patterns so as to permit the construction of atoms with the largest possible bond types. Only three spatial arrangements of fasteners are used, yet the number of possible bond types that can be constructed (*6*) exceeds that of any commercially available atomic and molecular models (see Table 2).

Table 2. Bond Types Which Can Be Constructed with the Molecular Orbital Models

Spatial arrangement of fasteners	Covalence	Bond type
Tetrahedron	2 to 4	Tetrahedral: sp^3, d^3s
Trigonal bipyramid	2 to 5	Linear: sp^3d
		Angular: ds
		Trigonal plane: sp^2, dp^2, d^2s, d^3
		S_N2 transition state
		Bipyramid: sp^3d, d^3sp
Octahedron	2 to 6	Linear: sp, dp
		Angular: p^2, ds
		Square planar: dsp^2, d^2p^2
		Octahedral: d^2sp^3

The atomic cores are colored, each bearing the color symbol of a specific atom. The colors used by the International Union of Crystallographers were chosen to symbolize each element: carbon, black; nitrogen, blue; oxygen, red; hydrogen, white.

The lobes representing the volume orbitals can be either colorless or matched to the colors of the atomic cores. In the construction of molecular models that are to stress the polynuclear orbitals, colorless lobes have been used. Lobes matching the color of the parent atomic core are chosen to draw attention to the individual atoms and their form of hybridization.

The modified thumbtack fastener permits the joining of the elements of the Molecular Orbital Models at any point and any desired angle or orientation in space, without the need of drilling permanent holes for the purpose. It is intended for use in the joining of molecules to depict their arrangement in crystals, or in portraying unusual bond angles or valencies.

With the help of the stick fasteners, the Molecular Orbital Models can be easily converted into a ball-and-stick molecular model set. The stick fasteners (Fig. 1) are graduated in decimal fractions of relative Angstrom units (5 cm = 1 Å) and can be adjusted to any required length, being built of two parts sliding in and out of each other. Only one type of fastener is therefore needed to represent any relative bond length. With these provisions it is possible to represent accurately relative bond distances, bond angles, and spatial orientation of molecular orbitals. The relative sizes of the molecular orbitals, however, as well as the relative sizes of the covalent cores, have only a schematic function when a ball-and-stick representation is chosen. The ball-and-stick variation of the Molecular Orbital Models is especially suited for classroom demonstration and for the study of optical isomerism.

Examples

Fully Saturated Molecules. This class is comprised of those saturated molecules that have no unshared electron pair orbitals capable of forming additional bonds. Methane, for example, is such a molecule.

This class is adequately represented by available commercial models as well as the Molecular Orbital Models and no further discussion is necessary.

Saturated Molecules with Unshared Electron Pairs. Water and ammonia belong to this class of molecules. Photographs of their Molecular Orbital Models are shown in Figure 2.

In the ammonia molecule three hydrogen atoms (white spheres) and an unshared electron pair (blue lobe) are arranged tetrahedrally around the covalent core (blue sphere in center) of the nitrogen atom. Two hydrogen atoms and two unshared electron pair orbitals are seen to occupy the four corners of the tetrahedron in the model of the water molecule (*7*, *8*). The

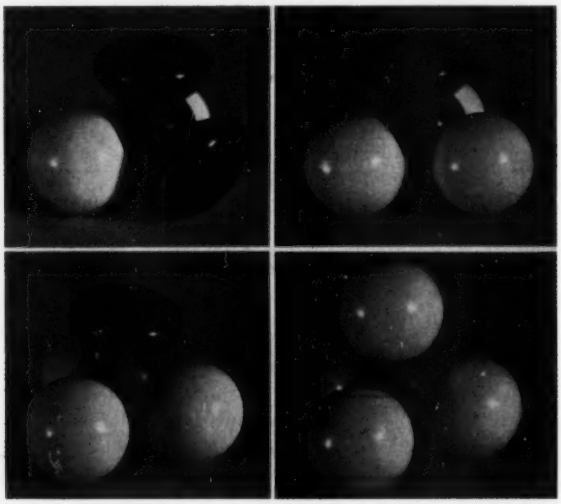


Figure 2. Neutral and protonated forms of water and ammonia. The water molecule (top left) is transformed into the hydronium ion (top right) by simply exchanging an unshared electron pair orbital cap for a hydrogen sphere. Similarly, the ammonia molecule (lower left) is changed into the ammonium ion(lower right).

unshared electron pairs, available for coordination, characterize bases. Models of the ammonium ion and of the hydronium ion result from the models of the molecule of ammonia and water respectively when an unshared electron pair lobe is exchanged for a hydrogen sphere. Thus only Molecular Orbital Models can be used to build models of carboxonium ions such as those reported recently by Meerwein, *et al.* (*9*).

Molecules with Simple pi Bonds. The Molecular Orbital Models are valuable in their ability to represent pi bonds. While the sigma bond is a sausage shaped, cylindrically symmetrical bond that does not occupy any additional molecular space aside from that already taken up by the covalent cores of the atoms, the double streamer pi bond located above and below the molecular plane contributes appreciably to the molecular volume. The difference between pi bonds and sigma bonds can be seen on the photograph of the model of allene ($H_2C{=}C{=}CH_2$) in Figure 3.

Especially noticeable is the large volume occupied by the two perpendicular pi orbitals, and the absence of cylindrical symmetry of the middle carbon atom. The model, in agreement with experimental evidence (*10*), also demonstrates the absence of conjugation between the two pi orbitals in allene.

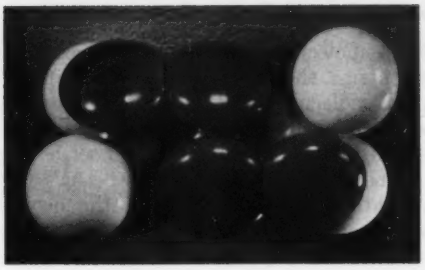


Figure 3. π-Bonding in allene. The model demonstrates the shapes and the relative volumes of the two π orbitals lying in two perpendicular planes. The overlap of the atomic *p*-orbitals forming the π bonds is represented by a meshing of the *p*-orbital lobes.

Molecules with Polynuclear Orbitals Extending Over More than Two Atoms. This class of molecules consists of two main groups, both characterized by a high resonance energy. The first group consists of aromatic molecules noted by the ring-shaped composite polynuclear orbital formed by a sextet of electrons. The second group comprises non-aromatic molecules that also have large polynuclear orbitals, none of which, however, closes to form a circle. To the latter class belong guanidines, amidines, nitrenes, amides of carboxylic acids, etc.

The most frequently encountered polynuclear orbital is the aromatic six-electron orbital which extends over rings of five, six, or seven atoms. An aromatic orbital can be seen in the photograph of the Molecular Orbital Model of the phenyl radical, ($C_6H_5\cdot$), in Figure 4. It can be seen that the unpaired (radical) electron is in an sp^2 orbital which lies in the nodal plane of the aromatic pi orbital. It follows that the interaction between the unpaired electron and a ring substituent can be due to induction but cannot be due to resonance.

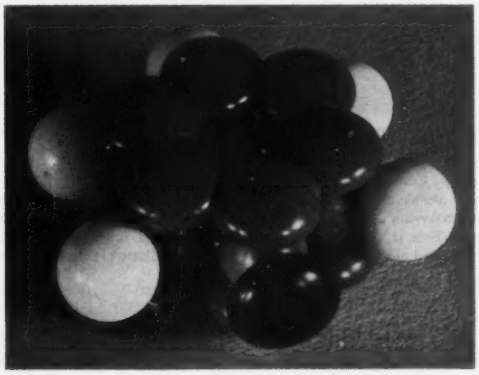


Figure 4. Phenyl radical. The geometric features of the aromatic π orbital and the sp^2 lone electron pair orbital are shown. In agreement with theory, the model suggests absence of conjugation between the double-streamer doughnut-shaped aromatic orbital and the orbital traced by the unpaired electron.

The guanidinium ion, $C(NH_2)_3^+$, (Fig. 5) is a non-aromatic molecule-ion that has a symmetrical polynuclear orbital resembling the letter Y (*11*, *12*). The orbital can be considered to be formed by the overlap of an imino pi bond with two unshared electron pairs on the two neighboring nitrogen atoms. It is of interest that urea, which has a Y-shaped polynuclear orbital analogous to the guanidinium ion, was found to have a resonance energy of 41 kcal/mole (*13*), a resonance energy larger than that of benzene.

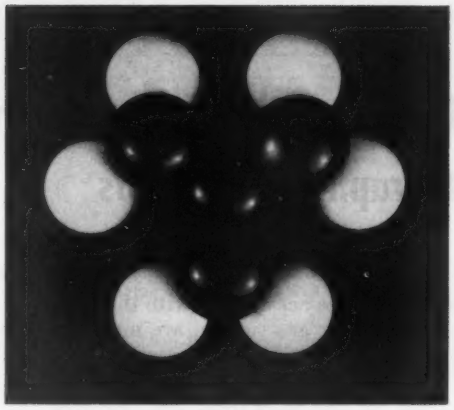


Figure 5. Guanidinium ion. The model brings attention to the polynuclear Y-shaped, double-streamer orbital—the cause of the planar structure of the ion-molecule.

The Hydrogen Bond. A simple replacement of an unshared electron pair orbital lobe with the hydrogen already bonded to another atom so as to keep the X . . . . . H-Y axis (where X may be the same atom as Y) as linear as possible, yields a model of a hydrogen bonded complex that correctly approximates the relative bond distances and bond angles, e.g., the model of the dimer of formic acid, $(HCOOH)_2$ (Fig. 6), is in agreement with the structure of the formic acid dimer as determined by the electron-diffraction method (*14*, *15*).

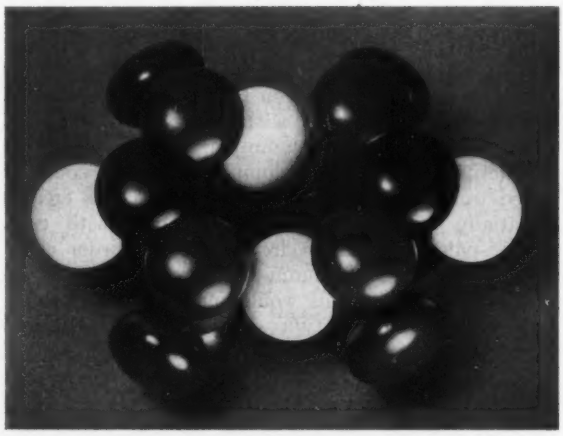


Figure 6. Dimer of formic acid. This model serves to illustrate hydrogen bonding in carboxylic acids. The protons of the hydrogen bonds are closer to one of the two oxygen atoms. The shape of the polynuclear orbital of the carboxyl group resembles the letter C.

The Uses of the Molecular Orbital Models

The models have been found useful in teaching undergraduate chemistry, in the study of the configuration and optical rotatory dispersion of atropisomeric biaryls, and in the investigation of the mechanism of organic and inorganic reactions.

The influence of the shapes, sizes, and spatial orientations of molecular orbitals upon the course of chemical reactions can hardly be exaggerated, and therefore a detailed representation of the molecular orbital structure appears desirable. In simple molecules it is possible to visualize or draw their molecular orbital structure and thus dispense with molecular models altogether. Working with larger molecules of simple structure, one can assemble their models from any of the conventional model sets, and mentally project the molecular orbitals into the loci where they belong. In large complex molecules, however, such as abound among the natural products (see for example the model of adenosine triphosphate, Figure 7) it would be a remarkable achievement to form a mental picture of the complex molecular structure including all its molecular orbitals and their relative orientation. We feel, therefore, that the Molecular Orbital Models are valuable in the investigation of biochemical processes.

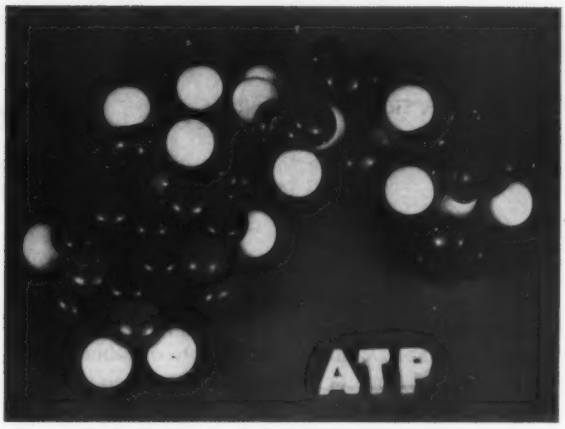


Figure 7. Adenosine triphosphate. The geometric features of the many possible interactions between the orbitals present in the molecule of adenosine triphosphate can be observed by twisting the model into the desired conformations.

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F. Sicilio[1], H. Bull, III,
R. C. Palmer, and J. A. Knight
Georgia Institute of Technology
Atlanta

An Inexpensive Versatile Multi-Column Gas Chromatograph for Students

A gas chromatography unit has been constructed in this laboratory from materials which are readily available with the exception of some of the electronic components and a matched pair of thermistors. A senior undergraduate student assembled this unit within one quarter as a special problem. The approximate cost of materials is $350, excluding recorder; this price can be reduced substantially by using materials normally on hand in a laboratory. Other home-made gas chromatographs have been described (*1–4*); the unit described herein incorporates features of added versatility and ruggedness. Experiments and specific applications in gas chromatography have been described (*1, 5*).

[1] Present address: A & M College of Texas, College Station, Texas.

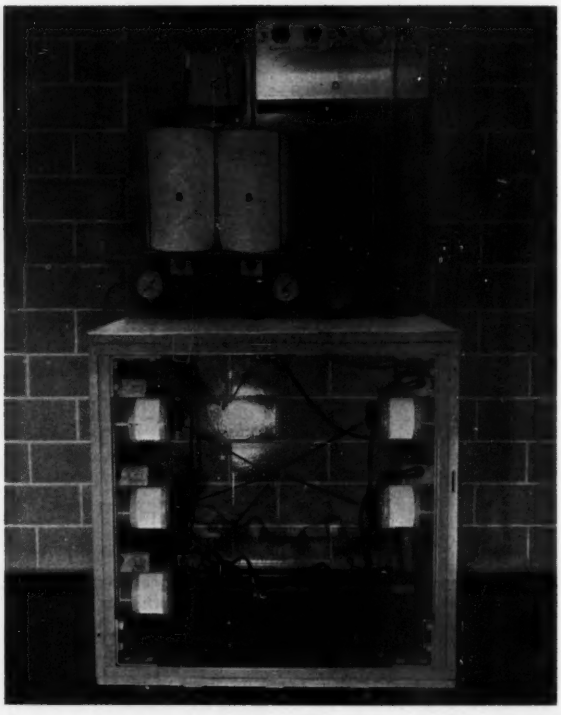

Figure 1. View of complete gas chromatographic unit with the exception of recorder. (A) Sample injection-flash evaporator units, (B) Column ovens, (C) Thermistor oven, (D) Control panel, (E) Soap-film flow meter, (F) Flow regulators, and (G) Variable auto transformers.

The unit and its accessories, with the exception of recorder and carrier gas supply, are mounted on a plywood platform provided with casters for portability (Fig. 1). As an alternative, the assembly could be compacted for use on a desk top. In this unit, two parallel columns are employed and are housed in separate ovens. Each column with its sample injection-flash evaporator unit is connected to one side of the thermal conductivity cell. Either column can serve as the preheater for the reference stream or as the chromatographic column. In essence, there are two parallel flows through identical systems, each of which consists of three major sections: sample injection-flash evaporator system, the chromatographic column and heater, and the sensing system. This arrangement enables the two columns to be packed with different materials, which permits different types of analyses to be accomplished without necessitating a change of columns or temperature. It is believed that the expense of the additional column is warranted because of the added versatility; however, the second column could be deleted in the interest of economy. A flow diagram for normal operation is shown in Figure 2. An extension of the two-column scheme is the preparation of a bank of column-pairs, each column-pair having a thermal conductivity cell. Each column-pair and cell could be added to the unit at small expense, and this creates essentially a new chromatographic unit with each column-pair. The same circuitry and recorder could be used then for any column-pair by use of a multiple-pole gang switch. This would make available to an analyst many different types of columns at any desired temperature, and all column-pairs could be equilibrated simultaneously. Other points of versatility are that columns of any practical length can easily be placed in the unit and the entire unit can be readily and conveniently disassembled. Also, the heating elements for the column ovens, thermistor block, and flash evaporators are controlled by individual variable auto transformers; this allows the use of many combinations of temperatures for instructional variety.

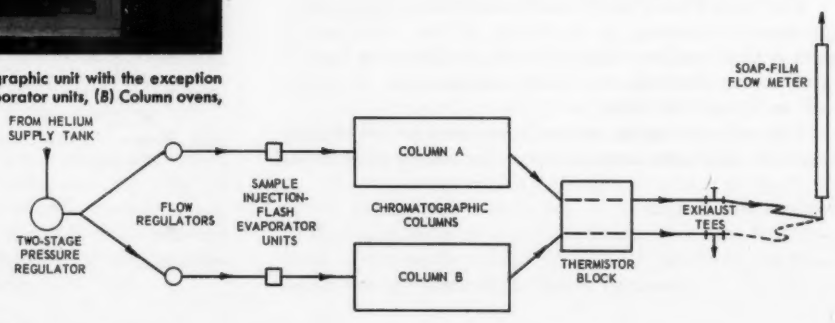

Figure 2 (right). Flow diagram for two-column unit. The sample can be injected into either stream. The other stream acts as a reference.

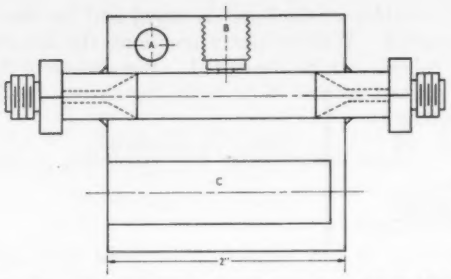

Figure 3. Brass flash evaporator unit, side section. (A) Well for thermometer, (B) Well for rubber septum, and (C) Well for cartridge heater.

The sample injection-flash evaporator unit is a brass block with a chamber and a side port through which the sample is introduced into the stream of carrier gas. The unit is heated by a cartridge heater and is insulated with asbestos paste and Flexboard. The unit is schematically shown in Figure 3. A sample can be introduced, with a syringe and hypodermic needle, through the perforated screw and rubber septum (Perkin-Elmer 154–1043). The sample injection unit also vaporizes liquid samples upon introduction to the chamber. The temperature of the chamber is measured by a thermometer placed in a well in the side of the brass block. The sample injection-flash evaporator unit is attached directly to the bottom of the column oven so as to eliminate cooling of the system at this point. The Swagelok fitting on the top of the injection chamber protrudes through the bottom of the column oven and is connected directly to one end of the column.

The coiled column is heated by an oven consisting of a 12-in. length of 4-in.-diameter steel pipe, nichrome heating element, and insulation. The steel pipe is first wrapped with asbestos paper to insulate the nichrome heating element. The outer asbestos insulation is wrapped in cheesecloth and is painted with a suitable coating (Sauereisen cement is satisfactory). The top and bottom of the oven are square pieces of Flexboard which act both as the structural body and as insulation. The temperature of the oven is controlled by manual setting of a variable auto transformer and is monitored with a thermometer, either partial immersion glass or bimetallic dial type. The temperature of the column itself is assumed to be approximately that of the oven, at reasonably low flow rates. Maximum usable temperatures, to the exclusion of column packing material, are in the order of 450°C.

The circuit diagram of the bridge is given in Figure 4. A matched pair of thermistors is used in combination with two 400-ohm resistors to form the basic bridge circuitry. Coarse and fine adjustments (10-turn precision potentiometers) are added to allow compensation for differences in flow rate, temperature, etc. The output signal is developed at the junction of the "sensing" thermistor and the resistor that forms that leg of the bridge. The junction of the other leg serves as a reference potential. Since the output signal of large samples is too great for a millivolt recorder an attenuator of precision resistors (Perkin-Elmer 154-0228) is used to decrease the output to the recorder by factors of two. The polarity of the signal reverses when changing from one thermistor to the other; therefore, a reversing switch is needed to provide upscale deflection when samples are injected into alternate columns. Power is supplied to the bridge by a 9-v battery (six $1^1/_2$ v cells in series). A 500-ohm variable resistor is used in series with the battery to allow adjustment of the applied potential of 8 v, which is monitored by a 0–10 v voltmeter. The bridge housing is easily removed for replacement of batteries. A null balance or potentiometric voltage recorder (5 millivolt or less), such as the Sargent SR or Leeds and Northrup Speedomax G, is utilized in conjunction with the bridge.

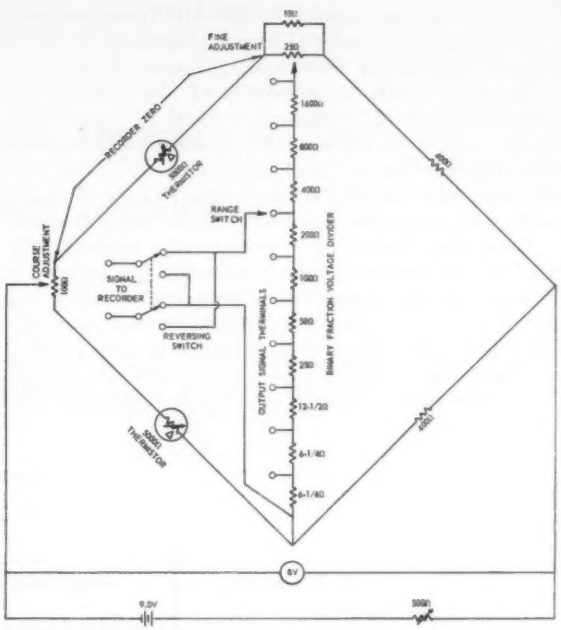

Figure 4. Circuit for bridge.

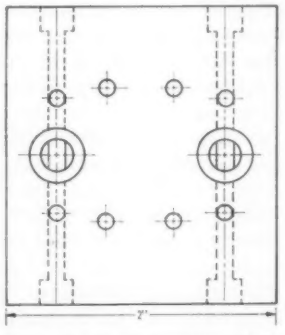

Figure 5. Steel thermistor block, top view.

The two thermistors (matched, Fisher Scientific, SPM 11-130-1-125) are housed in a steel block (Fig. 5). Each of the two streams of gases from the columns pass through the block by means of two parallel horizontal holes drilled lengthwise in the lower portion of the block. Vertical holes are also drilled through the top of the block into the center of each of the horizontal holes in the lower portion of the block. A shallow seat is also provided in the top of the two vertical holes. The thermistors, with their supports and electrical connections, are placed in these vertical holes. The thermistor support is a cylindrical piece of metal with the lower portion having the diameter of the vertical holes in the block. It is able to protrude slightly into the lower hole; the upper portion of the support has the same diameter as the seat. This upper portion of the thermistor support is made to bear on an "O" ring that is placed in the seat of the vertical hole to insure no leakage. The entrance and exit tubing of the thermistor block are made similar so that either end can be connected to the top of the columns. Thermal conduc-

tivity detectors are available for $60–$100 from firms such as Gow-Mac Instrument Company, Madison, N. J., or Victory Engineering Corporation, Union, N. J.

The oven for the thermistor block also employs the body-insulation of Flexboard as used in the column ovens. The oven is lined on four sides with nichrome wire which serves as the heating element. The outside terminals for the heating element of the oven are covered by a metallic guard to prevent electrical shock.

A soap-film flow meter is employed to determine the flow of the streams of gases through the two sides. The flow meter consists of a buret connected to one end of the run of a glass tee. A squeeze bulb, partially filled with soapy water, is attached to the other end of the run. The stream of gases, whose flow rate is to be determined, enters through the branch of the tee. The rise of a bubble in the buret is timed and the flow rate is calculated. With proper connections, the flow rate of either column can be measured. Regulation of flow is accomplished by use of pressure regulators (0–35 psi, Fisher 67581).

The authors acknowledge the assistance of Mr. D. K. Davis.

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(2) Sullivan, L. J., Lotz, J. R., and Willingham, C. B., *Anal. Chem.*, **28**, 495 (1956).
(3) Dimbat, M., Porter, P. E., and Stross, F. H., *Anal. Chem.*, **28**, 290 (1956).
(4) Gohlke, R. S., *Anal. Chem.*, **29**, 1723 (1957).
(5) Greene, S. A., J. Chem. Educ., **34**, 194 (1957).

S. F. Darling
Lawrence College
Appleton, Wisconsin

Demonstrating Enzymatic Hydrolysis of Glucosides by Paper Chromatography

The simple yet widely useful technique of paper chromatography is being introduced more and more into the introductory organic chemistry work.[1] Our students have used this technique to study sugar mixtures, to identify unknowns containing mono- and disaccharides and to identify amino acids in simple mixtures and protein hydrolysates. Instead of using the ascending techniques described in Fieser[2] we have employed the descending technique in large cylindrical or square glass jars equipped with glass trays and stainless steel holders.

One such square tank containing four trays gives space for students to develop 16 chromatograms each 4 in. × 22 in. This can be done overnight in a slow moving solvent mixture such as 10-3-3 butanol-pyridine-water or in a few hours with the fast moving solvent 9-2-2 ethyl acetate-acetic acid-water mixture. Both of these mixtures are well adapted for resolving sugars. For amino acid separation we have had excellent results with the 63-10-27 butanol-acetic acid-water mixture. (All the ratios quoted are by volume.) A 4-in.-wide strip of paper enables a student to spot his unknown together with two knowns or two known mixtures an inch apart at the start and still have the outer spots an inch from the edge. The last precaution avoids confusing effects associated with spots on the edge. Inexpensive but very satisfactory spotting tubes can be made from capillary melting point tubes drawn down to a much smaller diameter.

An interesting application of the use of paper chromatography is in the study of enzyme action. Simple β-glucosides are hydrolyzed cleanly and rapidly in the presence of β-glucosidase and this action is easily followed chromatographically using only micro amounts. In each of two 13 × 75-mm test tubes place about 5 mg of the glucoside salicin.[3] Dissolve each sample in about 1 ml of water. To the solution in one of the tubes add one or two milligrams of β-glucosidase.[4] After one hour spot a few microliters of the contents of each tube and a spot of glucose solution on the chromatographic paper. Develop this chromatogram either overnight in the 10-3-3 BuOH-pyridine-H_2O or two hours in the 9-2-2 EtOAc-HOAc-H_2O.

At the end of this time the chromatograms are removed from the tanks, the solvent front is marked and they are dried in the hood. The spots are brought out with modified silver spray.[5] Under the salicin in water alone should appear one spot for salicin at R_f about 0.62 in the 10-3-3 solvent mixture. Under the salicin with glucosidase should appear the prominent glucose spot at R_f 0.17 and salicyl alcohol at R_f 0.87, while complete hydrolysis is shown by the fact that no spot appears at the R_f of salicin. Under glucose there appears the prominent spot at R_f 0.17. If one desires, an extenstion of the experiment can be conducted as follows: Make duplicate chromatograms as described above. Spray one chromatogram with the modified silver spray and the other with diazotized *p*-nitraniline followed by sodium carbonate solution. This spray causes the salicyl alcohol spot under the hydrolysate to appear as a bright rose colored spot due to coupling action of the phenol with the diazonium spray. No color appears either under the glucose or the salicin in this case because of the inability of these substances to react with the diazonium spray.

[1] See, for example, this Journal, **37**, 49, 156, 293 (1960).
[2] Fieser, Louis F., "Experiments in Organic Chemistry," 3rd ed., D. C. Heath & Co., 1955.
[3] Arbutin can be substituted for salicin in which case both the original glucoside and the aglucone give colored spots with the diazonium spray.
[4] Obtainable from the Nutritional Biochemical Corp., Cleveland, Ohio.
[5] Pearl, I. A., and Darling, S. F., *J. Org. Chem.*, **24**, 735 (1959).

Lawrence F. Beste
E. I. du Pont de Nemours & Co.
Wilmington, Delaware

A Geometric Approach to the Gibbs-Duhem Equation

Nyburg and Halliwell[1] have made a valuable contribution to the teaching of chemistry with their geometric approach to extensive properties. We shall show that their method may be profitably extended to explain the application of the calculus to such problems. In particular, we shall use geometry to illustrate the derivation and application of the Gibbs-Duhem equation.

We consider an extensive property, such as the volume V of a system of two components at some constant temperature and pressure. In Figure 1 the volume is plotted vertically; the number of moles of the two components, n_1 and n_2, are plotted on the horizontal axes. As shown by Nyburg and Halliwell, the surface representing V is generated by a series of straight lines through the origin. The surface itself may be curved as shown in Figure 1. The point A represents $V_1°$, the volume of one mole of pure component 1; B represents $V_2°$.

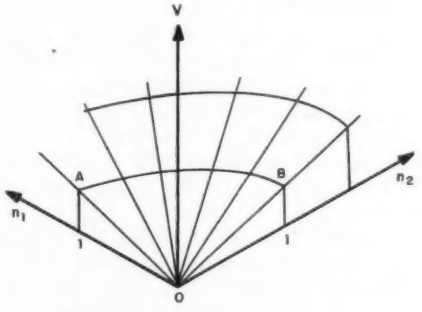

Figure 1. Volume of a system of two components.

We now ask how the volume changes when n_1 and n_2 are changed arbitrarily by an infinitesimal amount: that is, when n_1 is changed by an amount dn_1, and n_2 by an amount dn_2. This process is illustrated in Figure 2. We start with the volume V_A at point A. For the sake of brevity we shall say the volume equals A at point A, that is, the volume is given by the vertical distance of point A above the basal plane. As n_1 is increased by an amount dn_1, the volume increases to B. Thus, the increase in volume is $B-A$ or $B-A'$. We suppose for a moment that $\overline{AB}$ is a straight line. The slope of $\overline{AB}$ is *the rate at which the volume changes with respect to n_1 when n_2 is held constant.* In other words, the slope is the partial molal volume of component 1, $\bar{V}_1$; in terms of the calculus it is $(\partial V/\partial n_1)_{n_2}$. We can now state the following:

$$B - A' = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} dn_1 = \bar{V}_1 dn_1 \qquad (1)$$

In general, of course, $\overline{AB}$ will not be linear. However, it is shown in elementary calculus that equation (1) becomes true in the limit as the change in n_1 (and hence in V) becomes infinitesimally small; $B-A'$ then becomes dV. In a similar way V increases from B to C as n_2 is increased by an amount dn_2. The total change in V can now be given as:

$$dV = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} dn_1 + \left(\frac{\partial V}{\partial n_2}\right)_{n_1} dn_2 = \bar{V}_1 dn_1 + \bar{V}_2\, dn_2 \qquad (2)$$

In equation (2) dV is the *total differential* of V. The above exposition is not a rigorous derivation of dV, but it does provide an easy way to visualize dV and see what it means.

Relations Between Partial Molal Quantities

All the straight lines which form the volume surface in Figure 1 are lines of constant composition; that is, along any one line the ratio n_1/n_2 is constant. How can we write the equation of one of these lines?

We first note that as we proceed out from the origin along any line of constant composition we merely add more and more of the *same substance.* For example if we start with ethanol and water in the molar ratio 0.6/0.4 and add more ethanol and water in the same ratio, we will remain on the same line of constant composition. Every sample of such a mixture must have the same *intensive* properties as every other sample. It follows that the partial molal quantities will remain constant.

This being so, we may integrate equation (2) and

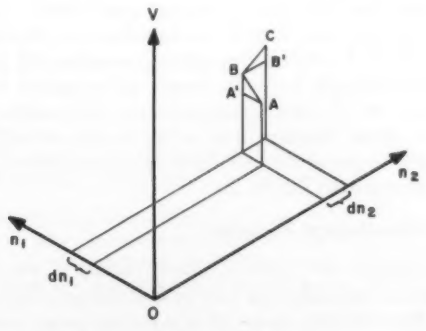

Figure 2. Change of volume with increase of n_1 and n_2.

[1] Nyburg, S. C., and Halliwell, H. F., J. Chem. Educ., **38**, 123 (1961). Note that on page 125 n_1 and n_2 were interchanged through a typographical error [see J. Chem. Educ., **38**, 329 (1961)].

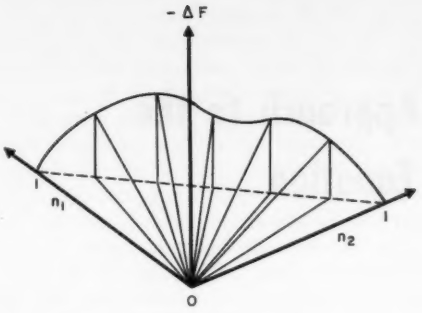

Figure 3. Free energy of mixing two components.

obtain the familiar result

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \tag{3}$$

It is to be noted that equation (3) applies only to one straight line on the volume surface with a constant ratio of n_1 to n_2. If we had the appropriate values of $\bar{V}_1$ and $\bar{V}_2$ we could in theory establish an infinite number of lines and obtain thus the entire surface.

It will be better not to perform this labor but to do something else. Imagining that we have established the surface, we may take the opportunity to walk about on it at will. That is, we need not keep to a line of constant composition but may let n_1 and n_2 vary independently. This will amount to differentiating equation (3) without holding $\bar{V}_1$ and $\bar{V}_2$ constant. The result is

$$dV = n_1d\bar{V}_1 + \bar{V}_1dn_1 + n_2d\bar{V}_2 + \bar{V}_2dn_2 \tag{4}$$

The dV we obtain in this way is the *total differential* of V and must be identical with dV in equation (2). It follows that the first and third terms on the right-hand side of equation (4) together equal zero. That is,

$$n_1d\bar{V}_1 + n_2d\bar{V}_2 = 0 \tag{5}$$

Of course, the intensive properties change only with a change in composition. To make this fact explicit we divide equation (5) through to obtain either of the two forms:

$$n_1\left(\frac{\partial\bar{V}_1}{\partial n_1}\right)_{P,T} + n_2\left(\frac{\partial\bar{V}_2}{\partial n_1}\right)_{P,T} = 0 \tag{6}$$

$$n_1\left(\frac{\partial\bar{V}_1}{\partial n_2}\right)_{P,T} + n_2\left(\frac{\partial\bar{V}_2}{\partial n_2}\right)_{P,T} = 0$$

The subscripts in equation (6) remind us that throughout this derivation we have been keeping to a constant pressure and temperature.

Equation (6) provides an extremely useful relation betweeen the two partial molal quantities. For example, if one has found an equation to express the variation of $\bar{V}_1$ with composition, equation (6) permits one immediately to write down an equation for the variation of $\bar{V}_2$ with composition. Equation (6) is one of those fundamental relationships which *must* be true; an apparent violation indicates there is something wrong with the data.

The Gibbs-Duhem Equation

To obtain the Gibbs-Duhem equation we merely start with the Gibbs free energy F instead of the volume. Since the absolute value of free energy is an indefinite quantity we are really interested in ΔF, that is, the free energy of the system minus the free energy of the components. Since ΔF is zero for either component, the ΔF surface includes the n_1 and n_2 axes (Fig. 3). Since Figure 3 applies to a realizable mixture, the value of ΔF is everywhere negative or zero. We plot the *negative* of ΔF in the figure, because the eye would be confused by a surface falling *below* the basal plane.

The partial molal free energy (or chemical potential) of component 1 is μ_1 corresponding to $\bar{V}_1$ in the volume case. Similarly, μ_2 corresponds to $\bar{V}_2$. Thus, one form of the Gibbs-Duhem equation can be obtained directly from equation (5) as

$$n_1d\mu_1 + n_2d\mu_2 = 0 \tag{7}$$

This important equation establishes a relation between the chemical potentials, μ_1 and μ_2. We shall want to follow this relation across an entire one-mole-total diagram from pure component 1 to pure component 2. But before we do this, we shall put equation (7) into a more convenient form.

We change n_1 and n_2 into mole fractions x_1 and x_2 by dividing through by $(n_1 + n_2)$. Letting x_1 be the independent variable, we obtain

$$x_1\left(\frac{\partial\mu_1}{\partial x_1}\right)_{P,T} + x_2\left(\frac{\partial\mu_2}{\partial x_1}\right)_{P,T} = 0$$

which is more useful after rearranging to

$$\left(\frac{\partial\mu_1}{\partial x_1}\right)_{P,T} = -\frac{x_2}{x_1}\left(\frac{\partial\mu_2}{\partial x_1}\right)_{P,T} \tag{8}$$

This equation is very useful for qualitative deductions as well as quantitative. For example, consider the case of the *ideal solution*[2] graphed in Figure 4. The equation for component 1 is

$$\mu_1 - \mu_1^\circ = RT\ln x_1 \tag{9}$$

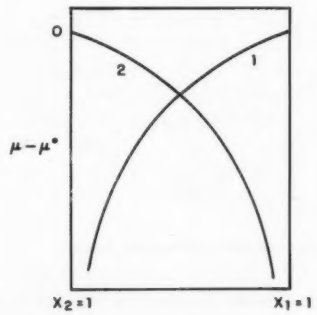

Figure 4. Chemical potentials in an ideal solution.

In equation (9), μ_1° is the chemical potential of pure component 1. The same equation, with change of subscript, applies to component 2.

Equation (8) tells us that where the slope of the curve for one component is negative, the slope for the other is positive; we see in Figure 4 that $\partial\mu_1/\partial x_1$ is everywhere positive and $\partial\mu_2/\partial x_1$ everywhere negative. Also, in accord with equation (8), the slope of each curve approaches ± infinity as the corresponding mole fraction approaches zero. Furthermore, where $x_1 = x_2$

[2] HILDEBRAND, J. H., AND SCOTT, R. L., "The Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Corp., New York, 1950, pp. 20–21.

in the center of the plot one slope is exactly the negative of the other.

It is still more interesting to consider non-ideal systems containing maxima and minima, such as the one graphed in Figure 5. Equation (8) tells us that where one component has a maximum (zero slope) the other will have a minimum (zero slope). These maxima and minima are usually the result of a large excess enthalpy of mixing. This follows because the partial molal enthalpy is zero for the pure component and tends to be maximum at infinite dilution. However, at infinite dilution the entropy dominates the curve as it approaches minus infinity; so a positive enthalpy can dominate only toward the center of the plot.

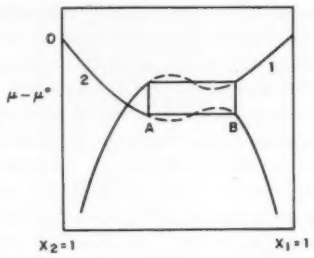

Figure 5. Chemical potentials in a mixture exhibiting phase separation.

A diagram such as Figure 5 warns us to expect phase separation. Component 1 can find two compositions (A and B) in which it has exactly the same chemical potential; at these same compositions component 2 also has equal chemical potentials. Any composition falling in the region where the curves are dashed will separate into two phases having compositions A and B. Phase separation indicates that the total free energy of the system is higher between compositions A and B than it is at A (or B). We see this condition in Figure 3, which is drawn for a system exhibiting phase separation. We follow the line across the surface (one-mole-total diagram) and find, starting from either axis, that the free energy first decreases, passes through a valley, goes over a hill and through another valley, and finally increases to the other axis. The two inflection points in the ΔF curve fall at exactly the same compositions as the maxima and minima in the corresponding curves for the chemical potentials (such as those in Figure 5). This becomes obvious when one recalls the intercept method for computing partial molal quantities from a one-mole-total diagram.

As another application of the Gibbs-Duhem equation we cite an example from polymer solution theory. The chemical potential of the solvent is usually expressed by the Flory-Huggins relation[3]:

$$\mu_1 - \mu_1^\circ = RT[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2] \quad (10)$$

In this equation v_2 is the volume fraction of polymer, x is the number of segments in the polymer chain, each of which is the same size as a solvent molecule, and χ_1 is an interaction parameter. The corresponding equation for the polymer is

$$\mu_2 - \mu_2^\circ = RT[\ln v_2 - (x - 1)(1 - v_2) + \chi_1 x(1 - v_2)^2] \quad (11)$$

Fairly recently, Tompa[4] brought equation (10) in better line with most data by adding an empirical term. His expression is

$$\mu_1 - \mu_1^\circ = RT[\ln(1 - v_2) + (1 - 1/x)v_2 + \chi_1 v_2^2 + \chi_2 v_2^3] \quad (12)$$

One might think at first blush that equation (11) should be similarly expanded by addition of $\chi_2 x(1\text{-}v_2)^3$, but the Gibbs-Duhem equation tells us this is not so. If χ_1 and χ_2 are to have the same values as in equation (12), then the proper expression for the polymer is

$$\mu_2 - \mu_2^\circ = RT[\ln v_2 + (1 - x)(1 - v_2) + (\chi_1 + {}^3/_2\,\chi_2)\, x\,(1 - v_2)^2 - \chi_2 x(1 - v_2)^3] \quad (13)$$

The most convenient form of the Gibbs-Duhem equation for checking the correspondence of equations (12) and (13) is

$$\left(\frac{\partial \mu_1}{\partial v_2}\right)_{P,T} = -\frac{v_2}{x v_1}\left(\frac{\partial \mu_2}{\partial v_2}\right)_{P,T}$$

Conclusions

Application of the calculus to extensive and intensive properties can be made clear and easy to remember by means of a geometric approach. The Gibbs-Duhem equation, an important and useful equation, is amenable to such treatment.

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[3] Flory, P. J., "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 495–518.

[4] Tompa, H., "Changements de phases," Société de chimie physique, Paris, 1952, pp. 163–5.

Volume III of Dreisbach's Physical Properties Series

"Physical Properties of Chemical Compounds—III" is the title of Number 29 in the "Advances in Chemistry Series."

The information is provided in the format adopted by the author, Mr. Robert R. Dreisbach, for his earlier compilations, originally prepared for workers in the laboratories of the Dow Chemical Company.

Volumes I and II appeared as Numbers 15 and 22 of the "Advances in Chemistry Series." The present work includes data on the physical properties of 434 aliphatic compounds and 22 miscellaneous compounds and elements. Of these, 22 are tables of improved values for compounds included in Volume II (Advances No. 22). This brings the total number of substances treated up to 1421. This volume also includes a combined index to the tables in all three volumes.

Copies can be ordered for $6.50 from Special Issue Sales, American Chemical Society, 1155 Sixteenth St., N.W., Washington 6, D. C.

William F. O'Hara,
Ching-Hsien Wu
and **Loren G. Hepler**
University of Virginia
Charlottesville

Temperature and Power Measurements in Precision Solution Calorimetry

It is our belief that research in solution calorimetry provides excellent training for undergraduates, even for those who have not yet formally studied thermodynamics or physical chemistry. Two accounts of calorimetric investigations carried out in large part by undergraduates at this institution have recently been published (*1*, *2*). In the course of this research several undergraduates have learned about precise electrical measurements, preparation and analysis of pure compounds, simple thermodynamic calculations, use of the chemical literature, and a little glass blowing. Finally, we believe that the undergraduates who have done solution calorimetry here have enjoyed it.

A few words about *some* of the kinds of solution calorimetry research that are suitable for undergraduates may be in order. Because of the limited time most undergraduates can devote to research and because even this limited time is often fragmented, we believe it is nearly essential that work be restricted to stable compounds so that compound preparation and analysis need not immediately precede the calorimetric work. It is also desirable to avoid explosive or highly toxic compounds.

Most of the calorimetric investigations so far carried out in this laboratory by undergraduates have involved determinations of heats of solution of inorganic solids in water or aqueous solutions. Results of these determinations have been used for calculation of partial molal entropies of aqueous ions and standard heats of formation of inorganic salts and of aqueous ions (*1*, *2*). There are many more similar heats of solution that can profitably be investigated. In general, we believe that such heats should be determined only for those compounds for which the data obtained can be used in some thermochemical calculation.

Investigations of heats of ionization of weak acids in aqueous solution, especially organic acids, are attractive for the undergraduate (or other) researcher. Some recent reports of investigations of this sort illustrate the calorimetric methods and the thermodynamic calculations that can and should be carried out (*3–11*).

There are many complex ion systems worthy of calorimetric investigation. If equilibrium constants for stepwise formation of the complex are known, it is possible but not often easy to obtain ΔH for each step. It is usually, however, relatively easy to obtain the total ΔH for formation of the complex ion that is formed in presence of excess ligand and it is this ΔH that is often most useful for thermochemical calculations. Most enthalpy data for complex ions have been obtained from temperature coefficients of equilibrium constants, but some data have been obtained calorimetrically (*12–15*).

It is apt to be more difficult to find suitable oxidation-reduction reactions for meaningful calorimetric investigation than to find suitable reactions or compounds for investigations of the kinds already mentioned. Many oxidation-reduction reactions in aqueous solution require high temperatures to proceed at a suitable rate; others are not quantiative or involve ill defined species. Nevertheless, oxidation-reduction reactions are well worth careful consideration because ΔH and especially $\Delta H°$ data for such reactions can be quite useful.

We have built a new calorimetric apparatus for precise measurement of heats of solution and heats of reaction in solution. Throughout the planning and construction of this apparatus we have given attention to making it reasonably inexpensive and also suitable for duplication and operation by undergraduates. Usually the greatest difficulty and expense in setting up for precision solution calorimetry is associated with temperature measurement; it is to this topic and to power measurements that this paper is mostly devoted.

Calorimetric Apparatus

A schematic diagram of our apparatus is given in Figure 1. Because the calorimeter is a Dewar vessel in only indirect contact with the water bath and because reaction periods are short (usually 0.5 to 5 minutes for heats of solution and about the same for many reactions), it is sufficient to control the bath temperature with a simple home-made mercury regulator and a commercial relay. It is easy to keep temperature oscillations down to about 0.02° in this fashion and with some care oscillations can be made smaller.

We have also found it satisfactory to control the bath temperature in another way. Room temperature is a little lower than the usual operating temperature of the bath so the bath loses heat to the room. The power input to an electric heater in the bath has been adjusted with a Variac until heat input nearly matches heat lost to the room. Short term temperature oscillations are thereby made insignificantly small but the bath temperature does tend to drift, often by about 0.05–0.08°/hour. A nearly steady drift of this magnitude does not adversely affect calorimetric investigation of rapid processes.

The constant temperature bath is always operated about 0.4° higher than will be reached by the contents of the calorimeter at any time during the experiment. This insures that all temperature-time drifts (dT/dt) will be of the same sign (positive). Further, it is desirable to have the top of the calorimeter and the

The financial support of the National Science Foundation and the Alfred P. Sloan Foundation is gratefully acknowledged.

exit tubes warmer than the contents of the calorimeter to minimize evaporation and condensation of the calorimetric fluid.

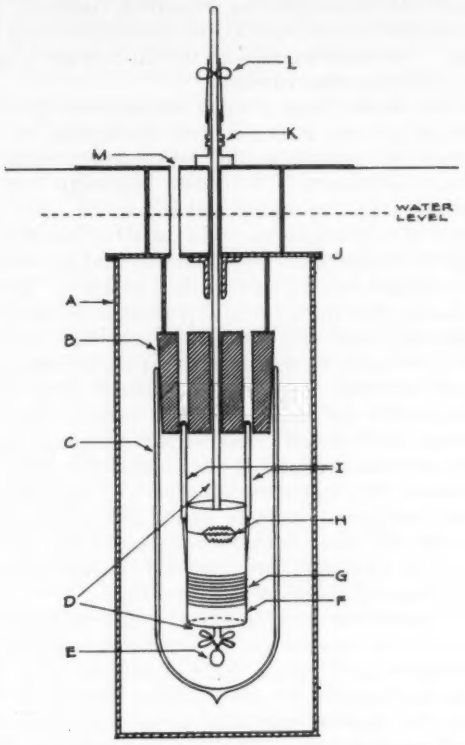

Figure 1. Schematic diagram of calorimetric apparatus. *A*, metal can; *B*, aluminum plug for Dewar; *C*, Dewar (with standard taper neck); *D*, home made pyrex stirrer; *E*, glass sample bulb, which is broken on bottom of Dewar to introduce the sample; *F*, silver or copper cylinder to which heater and thermometer are attached (this cylinder is covered with another cylinder and then painted with appropriate protective finish); *G*, heater; *H*, thermistors; *I*, stainless steel support and lead wire tubes; *J*, grooved flange, O-ring seal; *K*, pulley and bearing system connected to phonograph motor to turn stirrer; *L*, pinch clamp to hold or release stirrer; *M*, exit tube for heater and thermometer lead wires.

Temperature Measurement

The principal aim in choosing and designing a temperature measurement system was to secure sensitivity considerably better than 0.001° without excessively complicated construction and with minimum dependence on expensive instruments. We chose to base our system upon a potentiometer rather than a resistance bridge because a potentiometer is generally a more versatile instrument than is a resistance bridge and can readily be used in many physical chemistry experiments or for non-calorimetric research. Also, a good potentiometer costs less than does a good resistance bridge.

A brief account of our reasons for rejecting thermocouples or multiple junction thermopiles for temperature measurement is in order. A 50-junction thermopile gives about 20,000 μv/deg (μv = microvolt = 10^{-6}v), which can also be expressed as 5×10^{-5} deg/μv. When the cold junctions are at 0°C, the output of a 50-junction thermopile is $(2 \times 10^4\ \mu\text{v/deg}) \times (25\ \text{deg}) = 0.5$ v. Potentiometers such as the Leeds and Northrup K-3 and the Rubicon Type B have or approach microvolt sensitivity when the voltage being measured is small enough. "Small enough" is much less than 0.5 v. It is possible to avoid this difficulty and some others by making use of the twin calorimeter principle, but it is our belief that the many problems associated with proper construction and operation of twin calorimeters make this alternative incompatible with our aims. It might also be mentioned that construction of a 50-junction thermopile from fine wire is not a trivial task.

Several workers have described various modifications of the basic Wheatstone bridge circuit that permit precise temperature measurements with a resistance thermometer (*12*, *16*, *17*). None of these modifications adequately satisfied *all* of our criteria of simplicity of construction and operation and of inexpensiveness.

Thermistors are an obvious possibility for use in precise measurement of small temperature changes because of their large temperature coefficient of resistance and they have been used for this purpose in varous Wheatstone bridge circuits. We have had better success (at least with respect to our criteria) with a Maier transposed bridge circuit (*18*) adapted for use with commercially available thermistors and inexpensive resistors. A simple schematic of the Maier circuit is shown in Figure 2. Temperature sensing elements in this bridge have been made of copper by Maier and others (*19*, *20*). Sensitivity and measuring current data for two of the best Maier bridges are summarized in Table 1.

Table 1. Sensitivity and Measuring Current Data for Maier Bridges

Investigator	Sensitivity (deg/μv)	Measuring current
Southard (*19*)	1×10^{-3}	0.002 amp
Spedding and Miller (*20*)	3×10^{-4}	0.005 amp

Because dR/dT is larger for thermistors than for copper or other metals, better sensitivity than either of those quoted above can be obtained by substituting thermistors for the copper arms of the Maier bridge and this is what we have done. It is also possible to further improve the sensitivity by combining thermistors (dR/dT is negative) with copper or nickel (dR/dT is positive) in opposite arms of the bridge and putting all four elements in the calorimeter. Our experience has been that the extra improvement in sensitivity so achieved is not worth the extra difficulty associated with matching the resistances of the four arms.

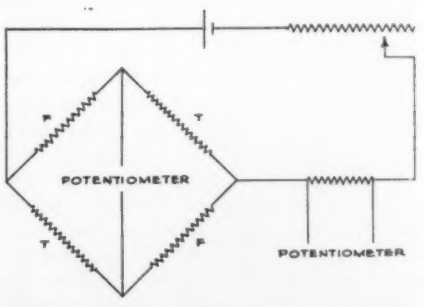

Figure 2. Schematic of Maier transposed bridge. Both *T*'s represent temperature sensitive resistances inside the calorimeter and both *F*'s represent fixed resistances outside the calorimeter.

We have used three Victory Engineering Corporation 1000-ohm thermistors (No. 31D34; $1.00 each) silver-soldered in parallel for each of the temperature sensitive arms of our bridge. This arrangement minimizes the i^2R heat developed in the thermistors by the measuring current and permits us to take advantage of the large dR/dT and small size of high resistance thermistors.

Our bridge circuit is shown in detail in Figure 3. Resistances of R_5 and R_7 were selected to make the potential measured by Potentiometer 1 (called E_1 hereafter) be positive above 24.6° and negative below 24.6°. Resistors R_1, R_2, R_3, R_4, and R_6 are from General Radio Company and cost $5.50 each. These resistors have low temperature coefficient of resistance.

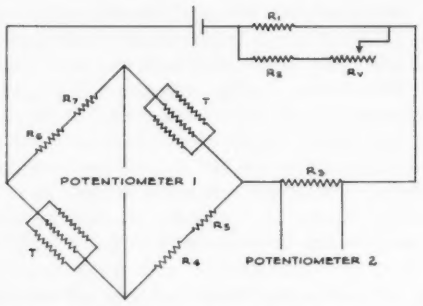

Figure 3. Detailed schematic of our Maier bridge circuit.
R_1 1,500 ohm resistor
R_2 20,000 ohm resistor
R_v decade box
R_3 300 ohm resistor (immersed in a can of oil)
R_4 and R_6 300 ohm resistors
R_5 and R_7 Resistors selected to make arms of bridge match at 24.6° (E_1 = 0), in this case about 40 ohms each
T thermistors immersed in calorimeter

Most of our work has been done with about 0.003 ampere measuring current from a 6-volt lead storage battery. The current is maintained constant to about 7×10^{-8} ampere, corresponding to E_2 maintained constant to within 2×10^{-5} volt by adjustment of R_v. Better apparent temperature sensitivities can be obtained by using larger measuring currents but this makes current control a little more difficult and is also undesirable because of heating of the thermistors.

Our bridge has been calibrated (0.003 amp measuring current) between 23 and 27°C by comparison with a mercury-in-glass thermometer previously calibrated at the Bureau of Standards. We found $dE_1/dT = 2.3 \times 10^4$ μv/deg at 25°C. Sensitivity is conveniently expressed as 4.3×10^{-5} deg/μv. This thermometer sensitivity is considerably better than sensitivities reported by earlier workers who used copper arms in Maier bridges (see Table 1). Our temperature sensitivity is comparable to that obtained by use of a Mueller G-2 bridge and is much better than that obtained with a Beckmann thermometer.

One mm deflection of the galvanometer used with Potentiometer 1 (1 meter light path) corresponds to 1.4 μv so our thermometer sensitivity can also be expressed as 6×10^{-5} deg/mm. This sensitivity can be improved by using an amplifier null detector, which is more expensive than a galvanometer, or by using a longer light path, which requires extra care to eliminate the effects of vibration.

Since our calorimeter was completed, Vanderzee and Myers (*21*) have described their new solution calorimeter in which temperature is followed with a thermistor bridge. They report sensitivity of 5×10^{-5} deg/μv with an unspecified measuring current. They also comment on the stability of the calibration of their bridge. Our experiences with thermistors are in agreement with their observations.

Several descriptions of other calorimeters have been published in THIS JOURNAL and comparison of these calorimeters (especially the temperature measuring systems) with ours is in order. Slabaugh (*22*) has described a fine calorimeter that can be used for a variety of investigations. He used a Mueller G-2 bridge for temperature measurement and had slightly better temperature sensitivity than we have. Because the Mueller G-2 bridge is an expensive instrument that is generally used only for temperature measurement with a resistance thermometer, temperature measuring systems like that described by Slabaugh (*22*) may be too expensive for many would-be users. The same objection can be raised to the temperature measurement system previously used in this laboratory (*23, 24*).

Mowery (*25*) and various others (*13, 26*) have described simpler calorimeters which are useful for some purposes, but their temperature sensitivities between about 0.01 and 0.001° are not good enough for proper investigation of many solution processes.

It is possible to use a *DPDT* switch so that the same potentiometer is used for measuring E_1 and also for periodically checking E_2. Our experience leads us to recommend against this arrangement because R_v must usually be adjusted right after a heating period or reaction period in order to bring E_2 back to the chosen constant value and it is desirable to be getting E_1 readings regularly and as soon as possible after drifts have become constant. We find this is best done when one operator uses Potentiometer 1 for E_1 readings and another uses Potentiometer 2 and adjusts R_v. It is, however, possible to check the potential drop across R_3 by balancing part of that drop against the potential of a standard cell, thus making it possible to get by in a reasonably convenient way with only one potentiometer.

Power Input and Measurement

The heater circuit (Fig. 4) has been made as simple as possible. The dummy heater is made of manganin wire wound on a copper tube enclosed in glass and immersed in oil. The calorimeter heater consists of

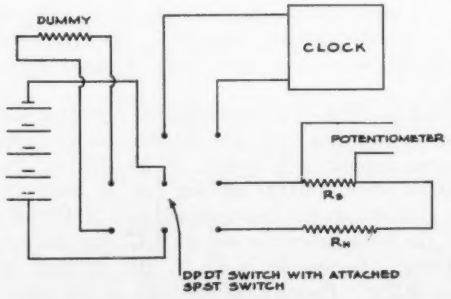

Figure 4. Schematic of calorimeter heater circuit. The potentiometer indicated above is also used to check the potential drop across R_3 (see Fig. 3).

about 200 ohms of No. 32 enameled manganin wire with No. 24 copper leads to binding posts on the top of the aluminum plate. Power for the heater is supplied by lead storage cells. The clock used is a Model S-10 from Standard Electric Time Company ($55) that is turned on when the triple pole switch is closed in the calorimeter heater position.

The calorimeter calibration heater should be of as high resistance as is practical. It is only in this fashion that lead resistance can be made nearly negligible with respect to heater resistance without using very large lead wires, which are undesirable because they are an excellent heat path in and out of the calorimeter. Further, it is easier to get a small constant current than a large constant current. We never use heater current larger than 0.2 amp and it is usually smaller

It is ordinarily unnecessary to use a constant frequency power supply (based on a tuning fork or other oscillator) to drive the clock motor because the local power company maintains frequency between 59.99 and 60.01 cycles/second most of the time with only occasional changes to 59.97 or 60.03 cycles/second. Our timing uncertainty in a one-minute heating period is not worse than 0.1%. A good stop watch can be used for most work; the uncertainty then is no more than about 0.3% for a one-minute heating period.

The heater circuit we use is satisfactory only if the effective resistance of the heater during a heating period can be adequately determined before or after the calorimetric experiment. This requires that the heater resistance must not change significantly with time nor with the temperature changes involved in the calorimetric experiment. Manganin wire is used so that dR/dT is small. Heat exchange with the calorimetric liquid is good so that the heater never gets very hot. It is verified by regular determination of the heater resistance that this resistance is nearly constant with respect to time.

The standard resistance used in the heater circuit has at various times been a one-ohm standard (Leeds and Northrup, $57) or a home-made manganin resistance standardized in terms of the one-ohm standard. The resistance of the heater has been determined by comparison with the one-ohm standard and also by comparison with a 100-ohm standard. The dummy resistance is made to match the sum of R_S and R_H to within two ohms.

Pitzer (*16*) has described a heater circuit involving a standard cell, some resistors (one variable) and a galvanometer. This circuit is more trouble to set up than is ours but may be more economical because it does not require a potentiometer.

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Substitute for Separatory Funnels

Marcel Jean
Université Laval, Quebec, Canada

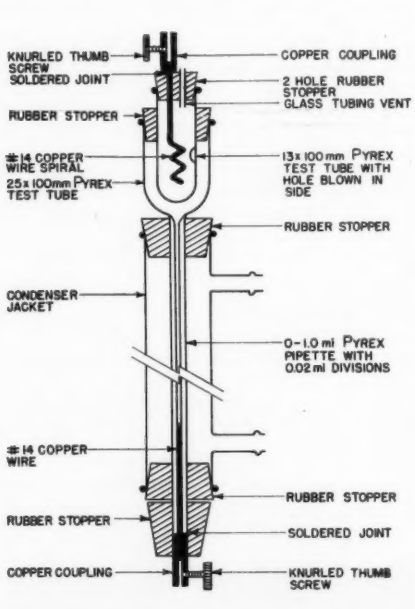
A convenient substitute for a separatory funnel can be made from a conventional polyethylene wash bottle by the simple device shown in the photograph. Cap *A* is the usual tight-fitting closure which can be used to seal the bottle during the shaking necessary to effect extraction. After the phases have separated, it is replaced by cap *B*. This is a wash bottle cap modified by cutting off the bottom of the delivery tube flush with the under surface of the cap. Squeezing the flexible bottle forces the liquid out of the bottle; pressure is released when the last drop of the desired phase has cleared the delivery tube tip.

Stephen W. Tobey[1]
West Virginia Wesleyan College
Buckhannon

Simplified Moving-Boundary Transference Cell

The transference cell shown in the figure is considerably easier to construct and operate than similar simple cells described earlier[2,3] for determining cation transference numbers by the moving boundary method, and the necessary materials for its construction will usually be readily available in any chemistry laboratory.

To prepare the cell for use, the upper (cathode) chamber is filled with the solution to be used in the experiment, a beaker is placed under the anode, and the anode stopper is momentarily loosened. The downward sweep of electrolyte effectively frees the capillary of any impurities or air bubbles present.



The cell has been used to determine the transference number of H^+ ion in dilute HCl solutions. Malachite Green Oxalate[4] indicator is more satisfactory than the usually specified Methyl Violet in these experiments because it does not decolorize. If a strip of white paper is taped to the back of the condenser jacket the ascending column of colored solution is much easier to see.

The predominate anode reaction during operation is

$$Cu \rightarrow Cu^{++} + 2e,$$

although the deposition of a small amount of a white precipitate on the tip of the anode during operation suggests that the reaction sequence

$$Cu \rightarrow Cu^{+} + 1e$$

$$Cu^{+} + Cl^{-} \rightarrow CuCl \downarrow$$

may also be occurring simultaneously. The mobilities of Cu^{++} and Cd^{++} are almost the same, so that no difficulty is created by substituting Cu for Cd in the anode. The cathode reaction is simply

$$2H^{+} + 2e \rightarrow H_2 \uparrow$$

Since this reaction takes place far removed from the capillary in which the moving boundary is generated, no complications due either to depletion of the catholyte in Cl^- or mixing of the solution by evolving H_2 arise.

Table 1 gives the results of a typical experiment performed using the apparatus described. The value of t_{H^+} calculated from this data is 0.806, to be compared with the literature value, 0.823.[5] Although circulation of constant temperature water around the capillary is not absolutely essential, the results obtained with thermostating were significantly better than those obtained on a prototype model which had only a large volume of water surrounding the capillary to act as a heat sink.

A convenient power supply for providing the necessary regulated current for this apparatus is described elsewhere in THIS JOURNAL.[6]

Table 1. Sample Experimental Results with 0.1022 M HCl at 25.0°C

$t_{(sec)}$	$V_{(ml)}$	$\Delta t_{(sec)}$
94	0.000	
		309
403	0.100	
		311
714	0.200	
		306
1020	0.300	
		302
1322	0.400	
		307
1629	0.500	
		304
1933	0.600	
		300
2233	0.700	
		306
2539	0.800	

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Stephen W. Tobey[1]
West Virginia Wesleyan College
Buckhannon

Constant Current Supply for Electrokinetic Experiments

The electronically controlled power supply described herein is designed to deliver the constant current required in electrokinetic experiments in physical chemistry. It is used in this laboratory in determining cation transference numbers by the moving-boundary method.[2, 3] In this particular application it performs the same function as a unit described earlier in THIS JOURNAL by Bender and Lewis.[4] However, the unit described below is based on quite a different operating principle and is consequently capable of delivering an appreciably more constant current over a considerably wider current range.

During an electrokinetic experiment, such as the determination of the transference number of a cation by the moving-boundary method, the electrochemical changes occurring within the transference cell may cause as much as a tenfold increase in the cell resistance as has been pointed out.[5] In the absence of any compensating action by the power supply being used, a tenfold decrease in the cell current would result. Since the cell current must ordinarily be maintained constant, some type of automatically compensating power supply is a practical necessity.

The circuit shown in Figure 1 will deliver any current from 1.0 to 10.0 milliamps to a load varying in resistance between 1 and 50,000 ohms, or up to 5.0 ma to a load varying between 1 and 100,000 ohms, with a total change in current delivered during a run of 1% or less without any adjustment. With only very occasional readjustment during an experiment, the current regulation can be held to within 0.2%.

To place the unit in operation, the cell or other load (R_L) is connected as shown and the unit is turned on. Negligible warmup time is required. R_5-R_6 is adjusted until the desired load current (I_L) is read on M_1. Final adjustment in I_L and minor readjustments during an experiment are made with R_4. Ordinary caution should be exercised in using the apparatus, since relatively high voltages are present at the output terminals.

Table 1 summarizes the performance of the unit under typical operating conditions. It also provides information on the calibration accuracy of the particular current meter used. The data were obtained by measuring with a potentiometer the voltage drop across a 100 ohm precision resistor connected in series with the indicated R_L. In obtaining the data, M_1 was set to the desired I_L with R_L equal to 10,000 ohms. The actual current delivered was measured, then R_L was increased and the measurement repeated. R_4 was not adjusted, except as noted.

Table 1. Performance of current regulator

M_1 reading milliamps	R_L ohms 10,000	50,000	100,000
	Measured I_L milliamps		
1.00	0.927	0.926	0.925
2.00	1.983	1.980	1.974
3.00	2.991	2.986	2.970
4.00	4.019	4.009	3.957
5.00	5.011	4.992	4.71 unsteady[b]
6.00	6.020	5.990	...
7.00	7.006	6.965	...
8.00	7.966	7.903	...
9.00	8.917	8.824 (8.920)[a]	...
10.00	9.853	9.733 (9.849)[a]	...

[a] M_1 reading obviously lower. M_1 reset to original reading with R_4.
[b] E_D required to maintain I_L constant reaches E_A (vide infra).

In further tests, a load of 25,000 ohms was placed on the unit and M_1 was set to 5.00 ma. The drift in I_L over a one-hour period was random ±0.02 ma. When the unit was plugged into a Variac and the line voltage varied between 120 and 100 volts ac, the resulting variation in I_L was ±0.03 ma.

The mechanism by which the circuit in Figure 1 maintains I_L constant despite changes in R_L is similar to that employed in constant-voltage power supplies,[5] and depends upon the fact that V_4 acts as a *variable resistor* which is automatically adjusted by the circuit to just offset any change in R_L. A detailed discussion of the mechanism by which the circuit operates follows. The functions and critical values of all components are given.

Assume that the unit is in operation, that R_5-R_6 has been adjusted to give the desired I_L, and that R_L is increasing with time. The necessary high dc voltage is provided by T_1, V_1, L_1, C_1, and C_2. T_1 should deliver approximately 750 rms volts. The current drain on the power supply is very low, so that by running V_1 as a half-wave rectifier the voltage at point A (E_A) is maintained at about +900 volts, close to the peak voltage output of T_1. V_1 must be able to withstand a peak inverse voltage of at least 2500 volts. R_1 is a protective resistor which discharges C_1 and C_2 when the unit is turned off. V_2 and V_3 are voltage reference tubes which in conjunction with R_2 provide constant voltages of approximately +75 and +225 volts at points B and C. The 110 volt ac input is run through the jumpers

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Parts List

C_1, C_2 4 mfd.
C_3 0.1 mfd.
R_1 500 K
R_2 50 K 10 watt
R_3 5K
R_4 2.5K potentiometer
R_5-R_6 100 K dual-section potentiometer. Ohmite type CCU 1041
R_7 10 K
R_8 1 Megohm
L_1 15 Hy. 75 ma
T_1 Stancor type P-8171
M_1 0-10 ma. dc milliammeter. Triplett model 420
S_1 SPST toggle switch
P_1 6.3 volt pilot light
F_1 1 amp fuse
V_1 5R4GY
V_2 OA3 (VR-75)
V_3 OD3 (VR-150)
V_4 6C5
V_5 6AU6

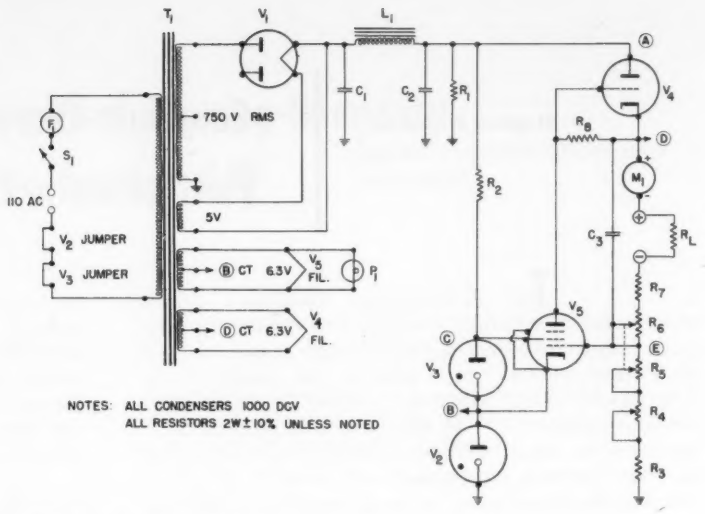


Figure 1. Circuit diagram of Current Regulator.

in V_2 and V_3 to prevent injury to V_5 if these tubes are removed.

As may be seen from Figure 1, E_A appears between point A and ground, and I_L (electron flow) passes serially through R_3, R_4, R_5-R_6, R_7, R_L, M_1, and V_4. R_3 and R_7 are protective resistors which prevent damage to M_1 if R_L is inadvertently shorted out. As R_L increases, the total resistance across which E_A is divided increases, and consequently E_E tends to fall below its normal value of +70 volts. As E_E decreases, the negative grid bias on V_5 increases above 5 volts since it is the difference between E_E and E_B, which is fixed at +75 volts by V_3. The increase in negative grid bias on V_5 results in a much amplified decrease in the current I_p flowing upward through R_3, the plate load resistor of V_5. Since R_3 also serves as the grid bias resistor for V_4, the negative grid bias on V_4 decreases, because the bias is generated by the flow of I_p through R_3. With decreasing grid bias, the internal resistance of V_4 decreases. This decrease in the internal resistance of V_4 exactly compensates for the increase in resistance of R_L and the net result is that I_L remains constant. The circuit responds equally well in the opposite direction to maintain I_L constant if R_L decreases.

The function of C_3 is to initiate a cycle of compensating changes identical to that described above in the event that transient disturbances occur in E_A, as would be caused by incomplete filtering of E_A or sudden changes in the line voltage.

The variation in internal resistance required of V_4 is quite large. In a typical electrokinetic experiment E_D increases from +200 to +700 volts, which with a typical I_L of 5.00 ma corresponds to a change in the internal resistance of V_4 of 100,000 ohms. The theoretical upper limit on the operating range of the circuit is reached when E_D equals E_A. This corresponds to the point where the internal resistance of V_4 goes to zero. However, V_4 has a critical minimum internal resistance below which it cannot decrease. When the internal resistance of V_4 required to maintain I_L constant falls below this critical value the circuit cannot function properly, and I_L falls, as is indicated in the last column of Table 1. The lower theoretical limit of satisfactory operation is reached when R_L is sufficiently small that V_4 is not capable of providing the necessary high internal resistance. However, this lower operating limit is never reached in the circuit shown because of R_6. When R_L is relatively low, the initial setting of R_5-R_6 required to bring I_L to the desired value automatically places most of R_5 in series with R_L, thus giving it a larger effective value. When R_L is relatively large, the required setting of R_5-R_6 to obtain the desired I_L automatically shunts most of R_5. A 6J5 may be used as V_4 with identical results. A 6AH4 as V_4 has a lower internal resistance and will slightly extend the upper operating limit. However its performance at low values of I_L is poorer. A triode connected 6F6, 6V6, or 6L6 will not operate satisfactorily as V_4 in this circuit. V_5 may be a 6AK5, 6AG5, or 954 with identical results. A 6SJ7 as V_5 provides poorer regulation.

The transformer shown (T_1) has two separate 6.3 volt filament windings with the center taps connected to points B and D. This maintains low filament-cathode voltages in V_4 and V_5. However, a prototype model with only one filament winding for both V_4 and V_5 with the center tap connected to point B showed no tendency to arc over in V_4.

The apparatus has been in use for some time and has given very satisfactory results. It should be pointed out that by suitably increasing the current and voltage breakdown values of a few key components the same circuit may be used to deliver much higher regulated currents than does the unit actually described.

An easily constructed transference cell for use with the apparatus described above in determining cation transference numbers is described elsewhere in THIS JOURNAL [6]

[6] TOBEY, S. W., J. CHEM. EDUC., **38**, 516 (1961).

Charles K. Mann and
Vernel C. Champeaux
Florida State University
Tallahassee

A Constant Current Source for Student Use

The development of electrochemical methods of analysis which utilize accurately controlled or constant direct currents has been very rapid in recent years. Examples of such methods are coulometric titration at constant current, potentiometric titration at constant current, chronopotentiometry, and current scanning polarography. These methods, particularly the first two, are very well suited for inclusion in the undergraduate instrumental analysis course.[1] It is the purpose of this paper to describe a convenient and inexpensive controlled current power supply which is well suited to use in a student laboratory.

Controlled current sources presently in use can generally be considered in three categories: dropping resistor, vacuum tube, and transistor. One type involves the use of relatively high dc voltage, e.g., 100 volts, a resistor, and the load, all connected in series. The resistor is very much larger than the load, so that nearly all the voltage is dropped through the resistor and small changes in load resistance have essentially no effect on the total resistance, hence, no effect on current. This type of power supply is the simplest to construct. It has the disadvantage of requiring frequent calibration. In addition, heating of the resistor with use must be taken into account. A second type involves the use of vacuum tubes. Many different designs have been described, frequently utilizing the flat plate current-voltage characteristic of the pentode. Vacuum tube power supplies, designed specifically for constant current coulometry or constant current potentiometry, are commercially available. They have the advantage of convenience, high precision, and large load tolerance; they are, however, quite expensive.

Use of transistors rather than vacuum tubes makes possible a power supply that is convenient and precise, but simple and inexpensive to build. To obtain an output current which does not vary with load changes, one makes use of the common base configuration.[2] In this configuration, collector current is directly proportional to emitter current within certain limits of load resistance. A transistorized instrument is simpler and less expensive than its vacuum tube counterpart because of its smaller power requirements. Small batteries with relatively long lifetimes and very high short term stability take the place of high voltage power supplies, which require fairly complex filters and voltage regulators to achieve necessary stability.

As usually built, the dropping resistor and the transistorized power supplies are battery-operated; accordingly, they provide extremely steady dc currents. By contrast, vacuum tube supplies are generally line-operated and show more or less residual ripple from rectification of ac. Comparing the two battery-operated types, the transistorized supply requires six volts; small, inexpensive batteries are sufficient. The dropping resistor supply generally uses about 100 volts, which requires larger and more expensive batteries.

The Instrument

A schematic diagram of the power supply is shown in Figure 1. It consists of one P-N-P transistor with two small dry cell batteries furnishing power. Battery "B_1," furnishing output current, is a 6v cell such as Eveready 510S. "B_2" in the emitter circuit is a smaller 1.5v cell, Eveready 950. "R_1" is a 2-watt wire wound potentiometer, the size of which is determined by the current output desired. "R_2," which is optional, serves to limit the range of output current, thereby simplifying close current adjustment by R_1. "S" is an SPST toggle switch. These components, together with suitable binding posts, are mounted on an aluminum chassis, 4 × 6 × 3 in. (Premier ACH 432).

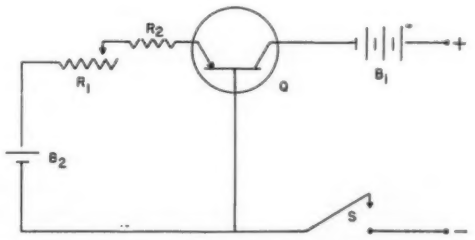


Figure 1. Schematic diagram of the constant current power supply.

Two types of these power supplies are used in this laboratory. One has a maximum current rating of 50 ma. It uses a Workman Power 6 transistor (Sylvania 2N68 is equally well suited, but more expensive). R_1 is 250 ohms; R_2, 47 ohms. With this arrangement, the instrument has a current range of 4 to 20 ma. The load resistance tolerance of this supply is increased by substituting a Tung-Sol 2N242, or equivalent, for the Workman Power 6. The low level source is rated at 10 ma. A G.E. 2N190 transistor is used. With R_1 of 3000 ohms and R_2 of 500 ohms, this instrument has a range of 0.36 to 2.40 ma. With

[1] Willard, H. H., Merritt, L. L., Jr., and Dean, J. R., "Instrumental Methods of Analysis," 3rd ed., D. Van Nostrand Co., Inc., New York, 1958, pp. 427, 508.

[2] Strobel, H. A., "Chemical Instrumentation," Addison-Wesley Publishing Co., Inc., Reading, Mass., 1960, p. 372.

R_1 of 10,000 and R_2 of 5000 ohms, the range is 87 to 250 μa.

All of the components used were obtained locally at a radio supply shop. Assembly is carried out with common shop tools and requires no special skill. The cost of all components is about $6.50 per unit for the low level or the high level supply with the Workman Power 6 transistor. Use of the 2N242 transistor adds about one dollar and larger batteries would increase the cost.

Performance

The effect of change in load resistance for the high level source is shown in Figure 2. Curve 1 pertains to the Workman Power 6 and curve 2 to the Tung-Sol 2N242 transistor. Using the Workman transistor with an initial current of 10 ma, the error amounts to less than ±0.5% at loads up to about 300 ohms. The tolerable load is larger at small currents and less at higher currents. For example, at 15 ma appreciable error is noted above 150 ohms. It may be noted that the IR drop in the load is approximately half the collector voltage.

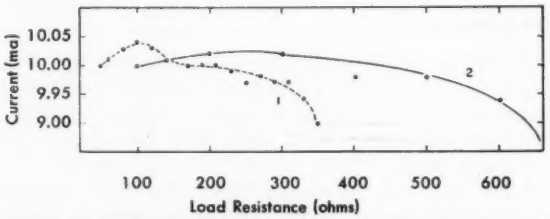


Figure 2. Change in Output with Load. Curve 1, Workman Power Six transistor; curve 2, Tung-Sol 2N242 Transistor.

With the 2N242 transistor, load tolerance is approximately doubled. With a 10-ma current, breakdown occurs sharply at 600 ohms. Power dissipation by this transistor is only a small fraction of the supply. Thus Ohm's law can be used to estimate load tolerance for a given collector voltage. This remains true at least up to 12 v furnishing 20 ma for which the tolerable load is 600 ohms. Since this transistor is rated to break down at 45 v and 2 amp, it should be possible to increase the load beyond 600 ohms at 20 ma by using larger collector voltages.

For reference, cell resistance under several conditions typically encountered in constant current coulometry are given to show order of magnitude. With two metallic electrodes (wire helix, about 2 × 3 cm) immersed in 0.2 *M* KCl, as would be the case for acid-base or argentimetric titrations, a resistance of 5 ohms was measured. When the electrodes were separated by a short salt bridge containing saturated KCl and one frit with 0.2 *M* KCl in the external solution, the resistance was about 50 ohms. The same arrangement with a salt bridge having two frits showed a resistance of about 80 ohms. With 1.0 *M*, rather than saturated, KCl in the double salt bridge the resistance was 150 ohms. Changing to 0.05 *M* KCl in the external solution with 1.0 *M* KCl in the double salt bridge gave a resistance of 220 ohms. These data indicate that it will generally be possible, with aqueous solutions, to use the high level current source with the Workman Power 6 transistor in the 10 to 15 ma range.

The low level current source showed measurable deviation only above 5000 to 10,000 ohms load. Since this is a far larger value than is likely to be encountered in aqueous solutions, no further investigation was carried out. The low level source should be useful with nonaqueous solutions as well.

To determine the effects of time, two different tests have been carried out. One involved allowing the high level source to discharge continuously through a load with periodic checking of the current. The result of this test is shown in Figure 3. After an initial drop, the current remains reasonably stable for about a week and then begins to drop off. The current was steady and with recalibration would have been usable at any time during the test period. At the end of the test the unit was still capable of providing 12 ma on readjustment of R_1. It would appear that for maximum stability, the instrument should be allowed to discharge for a while before calibration. The low level source would of course have a much longer life.

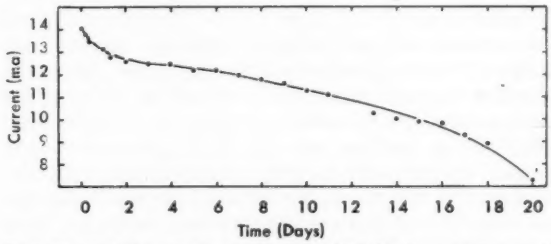


Figure 3. Variation of current with time. High level current source with 100-ohm load.

Under actual conditions of operation, current is delivered for only relatively short periods of time so that the batteries should have essentially shelf life. It was established that the current can be turned off and on repeatedly without change in calibration. At the current levels described here it is unnecessary to use a heat sink to prevent transistor heating. The instruments are calibrated periodically. Table 1 shows results of calibration of the low level source. The dial of the high level source does not permit highly reproducible settings of R_1.

Table 1. Calibration of Low Level Current Source

Time of calibration			
At assembly	After 23 days	After 42 days	After 58 days
0.0876*	0.0875		0.0833
0.1070			0.1068
0.1337			0.1322
0.1752			0.1748
0.2543			0.2554
0.362		0.362	
0.407		0.400	
0.443		0.442	
0.593		0.494	
0.560		0.559	
0.640		0.632	
0.753		0.748	
0.911		0.908	
1.138		1.134	
1.553		1.516	
1.876		1.849	
2.404		2.402	

* All currents measured in milliamperes.

The transistor power supply is very well suited to student experiments in constant current coulometry and potentiometry at constant current. With coulometric generation of titrant, any suitable end point can be used. The end point can be approached as slowly as necessary by repeatedly breaking the circuit. Time is most simply measured with a stopwatch. For best results, a precision electric timer is desirable. For potentiometry at constant current, the power supply is connected to the electrodes in parallel with a vacuum tube voltmeter. This arrangement is useful either when a *p*H meter with constant current feature is unavailable or when the single current value provided by a meter is unsatisfactory. In addition, these supplies provide a source of small dc current and voltage for general use in the laboratory. For example, with a known resistance it makes a convenient calibrator for variable span potentiometer recorders.

Acknowledgment

The writers wish to thank Warren Cloer, Ronald Dapo, and John Motes for some of the measurements.

Robert Barnard
and **Ray Woodriff**
Montana State College
Bozeman

A Low Cost Direct Current Source for the Laboratory

The need for a low cost source of variable direct current has been satisfied by the unit described in this article. Originally designed to furnish a maximum of 6 volts dc and up to 3 amps for electrodisposition experiments, these power supplies have also been used in place of batteries when performing oxidation-reduction experiments. The units require only a single 110 v outlet for operation and hence can be carried to the students' work area.

The apparatus consists of the power supply, a magnetic stirrer, and platinum electrodes. The advantage of the removable magnetic stirrer is that it can be detached for other uses and makes for a lower over-all investment in equipment, since the two units may not always be used together.

The power supply consists of a full wave selenium industrial rectifier stack and selenium rectifier transformer, controlled by a powerstat auto-transformer across the 110 v ac line input. The 3 amp output meter is protected by a 3 amp fuse. Since the ammeter is a current averaging device, no filtering of the rectified output is necessary. This reduces cost to a minimum (about $40) by keeping circuitry as simple as possible.

The upright posts for carrying the dc current are made of copper tubing soldered to nuts which can be threaded onto insulated studs attached to the base. These can be removed for easier storage. The adjustable clips on the parts are bicycle pants clips with holes punched in them to allow them to slide on the uprights (Fig. 2).

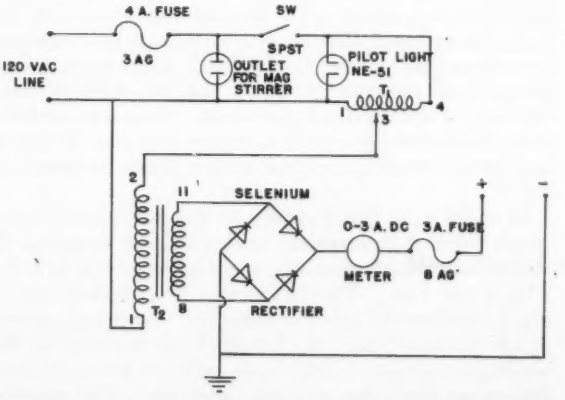


Figure 1. Circuit diagram. T_1 = Powerstat autotransformer, Type 10. T_2 = Stancor power transformer, RT 202. Selenium rectifier, type 310, Allied Radio #4A789. Meter 0–3 amp $2^1/_2$-in. rectangular, Simpson. Neon indicator light, Dialco Type 937 has built-in resistor for Ne 51 Neon lamp in 110 v ac circuit.

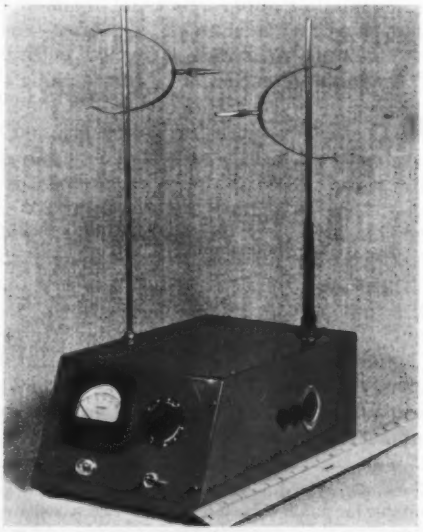


Figure 2. Power supply with mounted binding posts: removable magnetic stir sits in between posts on top of cabinet and plugs into outlet on the side.

We acknowledge the assistance of the Electronic Research Laboratories at Montana State College, which contributed the circuit design of the power supply and constructed the units.

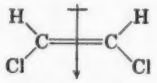
GUEST AUTHOR
Wilbur N. Moulton
Southern Illinois University
Carbondale, Illinois

Textbook Errors, 34

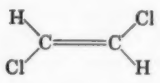
Dipole Moments of Symmetrical Organic Molecules

The use of dipole moments to assign *cis* or *trans* configurations to olefins is frequently introduced in elementary organic textbooks.[1] The method is a useful one in some cases, but it is not applicable to all olefins. Some of the problems and limitations involved also arise in considering the dipole moments of substituted benzenes.

The example which is most frequently given is 1,2-dichloroethylene, in which case the dipole moment (μ) of the *trans* isomer is zero and that of the *cis* isomer is about 1.85 Debye (D). The dipole moment of a molecule is the resultant of the group moments treated as vectors. As shown below in *cis*-1,2-dichloroethylene the resultant, primarily the vector sum of the carbon-chlorine moments, is perpendicular to the carbon-to-carbon bond and in the plane of the molecule. In *trans*-1,2-dichloroethylene the carbon-chlorine moments are directed in exactly opposite directions, and therefore the vector resultant is zero.

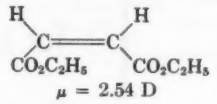


μ = 1.85 D

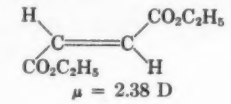


μ = 0

No error is involved in this special case, but there is when it is stated or implied that the dipole moment of all symmetrical *trans*-olefins will be zero. The dipole moment of symmetrical *trans*-olefins will be zero if, and only if, the group moments are directed along the axes of the bonds from the olefin carbons to the attached groups. Groups for which this is true are said to have axial or linear moments, and include hydrogen, the halogens, nitro, nitrile, and methyl groups. A second class of groups have moments that are not directed along the bond axis. In these cases the group moments for the *trans* isomer are not at an 180° angle from each other, hence the vector sum is not zero and the dipole moment is not zero. Groups of the second class include hydroxyl, alkoxyl, amino, carboxylic acid, ester, aldehyde, and ketone groups. Maleic acid and fumaric acid constitute a case of *cis-trans* isomerism in which the groups attached to the double bond do not have axial moments. This case is complicated by hydrogen bonding in the free acids, but the dipole moments of the diethyl esters have been measured. The observed dipole moments are 2.54 D for diethyl maleate and 2.38 D for diethyl fumarate. Although the dipole moment for the *cis* isomer is greater than that for the *trans* isomer, the small difference between two large dipole moments would not be adequate basis for assignment of configuration.

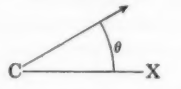


μ = 2.54 D



μ = 2.38 D

The angle (θ) between the bond axis and the bond moment can be calculated from experimental data and varies from 55° for methoxyl to 142° for the amino group attached to aromatic carbon. The calculated angle between the bond axis and bond moment for a given group are not necessarily the same in aliphatic compounds as in aromatic compounds. A value of



θ greater than 90° indicates that the group is positive with respect to the rest of the molecule to which it is attached.

An error more frequently made by implication than by direct statement concerns *para*-disubstituted benzenes. It is often pointed out that *para*-dinitrobenzene has a dipole moment of zero, which is true as it is of all other cases in which two like groups with axial or linear bond moments are *para* to each other. From the discussion above it is obvious that it cannot be correctly assumed that all *para*-disubstituted benzenes have zero dipole moment. Rather in all cases involving groups with non-axial moments the *para*-disubstituted benzenes will have dipole moments. Examples include *para*-diaminobenzene with a dipole moment of 1.5 D and *para*-dimethoxybenzene with a dipole moment of 1.7 D.

It might seem that if groups are free to rotate about a single bond[2] that variously oriented dipole moments of the different conformations might average out to zero. This is not true. The fact is that if a molecule has a dipole moment in any conformation it will have a net dipole moment, since the actual dipole moment is the weighted average of the dipole moment for each conformation that the molecule assumes. The experimental dipole moment falls between the values calculated for the conformations with maximum and minimum dipole moment. In *para*-dimethoxybenzene two important conformations are shown. It can be

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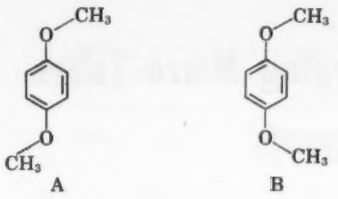
Suggestions of material suitable for this column and guest columns suitable for publication directly are eagerly solicited. They should be sent with as many details as possible, and particularly with references to modern textbooks, to Karol J. Mysels, Department of Chemistry, University of Southern California, Los Angeles 7, California.

[1] Since the purpose of this column is to prevent the spread and continuation of errors and not to evaluate individual texts, the source of errors discussed will not be cited. To be presented, the error must occur in at least two independent standard books.

argued that resonance interaction of the oxygen with

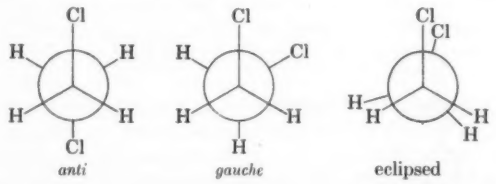


A B

the ring would favor such planar conformations. Of these conformers *A* would have zero dipole moment and *B* would have a large dipole moment. The experimental value (which is smaller than that calculated for *B*) can be explained if one assumes that *para*-dimethoxybenzene exists as a mixture of the two. However, there is nothing about the experimental data that requires planar conformation. Completely free rotation about the carbon-oxygen bond is not ruled out by the dipole moment data.

The treatment of free versus restricted rotation is not limited to aromatic systems. An examination of this problem in an aliphatic system, in addition to its own merit, can be used to correct another error. A recent textbook states that any molecule that has a center of symmetry will not have a dipole moment. A current monograph implies the same argument by stating that hexamethylenetetramine does not have a dipole moment because it has a center of symmetry. The fact is that the presence of a center of symmetry does not necessarily prevent a molecule from having a dipole moment. In the case of hexamethylenetetramine the molecule does not have a dipole moment, but neither does it have a center of symmetry.

The case of 1,2-dichloroethane will illustrate the point. This compound can exist in a number of conformers of which three are shown.



anti *gauche* eclipsed

The eclipsed conformation shown and other eclipsed conformers in which chlorine and hydrogen are eclipsed are too unstable to make any appreciable contribution, so only the *anti* (also called *trans* or staggered)[2] and *gauche* (skew) conformers need to be considered. The *anti* conformer in addition to a plane of symmetry has a point of symmetry, and since the bond moments are aligned in such a way as to have a vector sum of zero, the dipole moment would be zero for this conformer. However, the *gauche* conformers, the one shown and its non-superimposable mirror image, are not symmetrical and would have a dipole moment and optical activity if each were treated independently.

Experimentally, a dipole moment of 1.12 D at 32°C and 1.54 D at 271°C is observed for 1,2-dichloroethane, and the compound is optically inactive. This can be explained by assuming that the observed dipole is the weighted average of that for each of the various conformers, the *anti* conformer predominating at lower temperatures. As the temperature increases the internal energy of the molecule increases and more of the molecules assume the *gauche* conformation. The value at 271° has been calculated to be about that which would be expected for a random distribution between the *anti* and the two *gauche* conformations. The molecule is optically inactive because there are an equal number of each of the two non-superimposable *gauche* conformers.

The following general rules relate conformation, optical activity, and dipole moment. If any of the conformers in which a molecule can exist has a center of symmetry the compound will be optically inactive. If any conformer has a dipole moment, the compound will have a dipole moment. A compound will not have a dipole only if the center of gravity of negative charge coincides with the center of gravity of positive charge in all conformers. It would seem that even a minimum treatment of the topic should include these basic principles in some form.

The data used in this article and excellent treatments of the topic can be found in the books listed in the bibliography.

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[2] For a discussion of the principles of conformational analysis see ELIEL, E. L., J. CHEM. EDUC., **37**, 126 (1960).

New Book Lists Free Materials

Thomas J. Pepe, Superintendent of Schools in Southbury, Connecticut, and a committee of educators have selected and evaluated the educational aids offered by firms and foundations. Their conclusions are available in the volume, "Free and Inexpensive Educational Aids," Dover Publications, 180 Varick Street, New York 14, N. Y., $1.35. Designed to meet the needs of students, teachers, and audio-visual directors, this book can be used by anyone interested in obtaining quality educational materials.

The book lists more than 1500 items organized into 59 categories, which Mr. Pepe and his staff have judged to be informative, objective, and educationally sound. Each entry includes information on the presentation, quality of contents, and grade level.

John T. Stock, M. A. Fill
and R. G. Bjork
University of Connecticut
Storrs

Device for Charging Micro-Tubes with Toxic Reagents

By use of the "air flow" or "aspiration" technique, toxic volatile reagents such as phosgene and nitrogen dioxide may be safely and easily handled on the microchemical scale.[1] On this scale, such reagents are conveniently stored in ordinary soft-glass melting-point tubes, both ends of which are sealed. Since such tubes, each of which contains about 25 mg of reagent, may be broken right inside the reaction assembly, preparations involving the use of these reagents may be tackled by comparative beginners. The operations are conducted under slight water-pump suction, so that any reagent excess is carried down the sink and does not get into the laboratory atmosphere.

An apparatus that permits batches of tubes to be rapidly and safely charged with phosgene, etc., is shown in Figure 1: Side arm *A* is connected to a mercury manometer and through a stopcock *B* (not shown) to a suction reservoir. This is a large empty bottle that is partially evacuated by means of a water-pump. For ease of manipulation, the plugs of *B* and of the air-inlet stopcock *C* should be modified to give a finely-controllable opening.[2] To limit the maximum rate of air entry, a capillary leak (not shown) is attached to *C* by means of a sleeve of rubber tubing.

Since the interior of the apparatus cannot be inspected when partially jacketted for the handling of phosgene, it is desirable to make a preliminary run with an easily-handled liquid such as colored water. This enables the length of the liquid column that enters the tubes during charging to be visually related to the change in manometer readings. The column length in charging operations which cannot be directly observed may then be gauged approximately.

The completely dried apparatus is assembled in a fume hood. Except as a precaution, the draft need be on only when liquid phosgene is being introduced from a lecture-size cylinder. The lower portion of phosgene reservoir *D* is immersed in solid carbon dioxide contained in a well-lagged beaker. Ice or ice and salt may replace solid carbon dioxide when reagents of lower volatility are to be handled. Container *E* and the rising portion of siphon *F* are similarly refrigerated. This may be done by means of a polyethylene candy-bag, which is slipped into the position indicated by broken lines and is partially filled with solid carbon dioxide or other refrigerant. Liquid phosgene (3 to 5 ml) is then run into *E*. About a dozen melting-point tubes (only one is shown), each of which is closed at one end, are placed mouth-down in holder *G* and the latter is carefully pushed home. Four narrow slits at the bottom of *G* allow entry and egress of liquid. When assembly is complete, stopcocks *B* and *C* are closed, the three-way stopcock *H* is turned to position (*a*) and the suction reservoir is pumped down.

Stopcock *B* is slightly opened so that the pressure within the apparatus slowly falls to about 100 mm; *B* is then closed and *C* is slightly opened to allow slow entry of air. As this enters the apparatus, phosgene rises in the tubes in the holder; by closing *C* at an appropriate manometer reading (about 250 mm), the desired column-length within the tubes may be obtained. After closure of *C*, stopcock *H* is turned to position (*b*) and stopcock *B* is slightly opened so that suction is applied through hole *I* to the phosgene reservoir. Unused phosgene commences to rise in the siphon and, as soon as the liquid has passed the bend and started downwards, stopcock *B* is closed and *H* is turned to position (*c*). When the level of the liquid has fallen below the bottom of holder *G*, stopcock *C* is opened to allow the interior of the apparatus to come up to atmospheric pressure. Excess of phosgene passes into *D*, while the columns recede well away from the open ends of the melting-point tubes.

Having withdrawn the tube-holder, its contents are at once tipped into a short refrigerated flat-bottomed vessel *J* as shown in Figure 2. A pad of asbestos paper

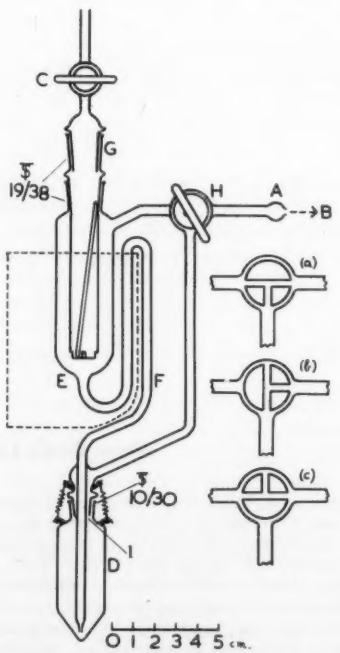


Figure 1. Apparatus for charging tubes.

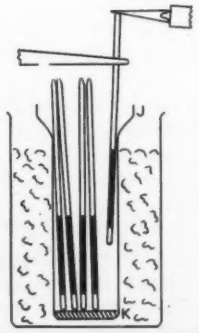


Figure 2. Technique for sealing charged tubes.

[1] See, for example, Stock, J. T., and Fill, M. A., J. Chem. Educ., **32**, 586 (1955).

[2] Stock, J. T., and Fill, M. A., *Analyst*, **71**, 142 (1946).

K eliminates the slight risk of breakage during transference. In turn, each tube is picked up by tweezers as shown and is at once closed with a touch of small hot flame. Sealing is simple and rapid if the mouths of the tubes are reduced in diameter by partial drawing-out as indicated in Figure 2. This operation is of course performed before the tubes are filled.

A further batch of empty tubes is loaded into the holder, which is restored to its normal place. Stopcock C is then closed and, leaving H in position (c), B is partially opened. Liquid is thus drawn up from the reservoir into the container. Stopcock H is then returned to position (a) and the slow fall in internal pressure is allowed to continue. After inspecting one or two of the first batch of tubes, the filling and sealing operations are continued. If the tubes are judged insufficiently filled, the first air-inlet stage should be continued to a pressure somewhat higher than that used for the first batch. With over-filled tubes, air-inlet should be cut down.

This apparatus was developed with the partial support of the National Science Foundation's Undergraduate Research Participation Program.

G. O. Pritchard
and **G. H. Miller**
University of California
(Santa Barbara) Goleta

Safety Device for Vacuum Diffusion Pumps

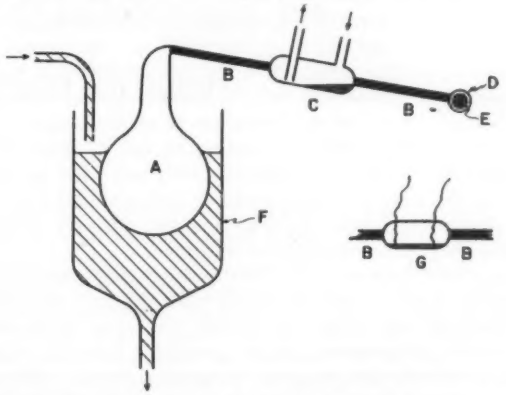
Mercury or oil diffusion pumps in any vacuum system are dependent on a steady stream of coolant water for safe and efficient operation. Any interruption of the flow of water can be used to activate safety devices for the control of the diffusion pump heater.[1–4] A commercial device[5] which operates on a diaphragm principle is commonly used to protect spectrophotometers but can also be used for electrically heated pumps.

The device described herein is one that can be assembled easily and is fully automatic in that the heat source is reactivated if the flow of coolant water is resumed.

If the diffusion pump is heated with a Bunsen burner, a suitable arrangement is shown in the figure. A is a 100-ml round-bottom flask. B is solid glass rod, supporting the glass attachment C. D is a short piece of glass tubing which pivots on a fixed metal rod E. F is a 250-ml beaker, drawn off as shown, and the outlet to the drain is so regulated that the bulb A floats close to the top of the beaker with a suitable rate of flow of water from the outlet of the condenser of the diffusion pump.

The gas flow to the Bunsen burner in normal operation passes through bulb C. The small pool of mercury in C stays at the right hand end when the arm BCB has a downward cant. If the water supply from the diffusion pump diminishes, the level in the beaker drops, and so does A and the arm BCB. This causes the mercury to run to the left hand end of C which covers the mouth of the small exit tube and cuts off the gas supply (the gas pressure is insufficient to blow mercury into the room). A small pilot light (insufficient to heat the pump) mounted next to the Bunsen burner relights the gas flame if the water supply should be resumed, when A rises to its former level, and the gas has free passage through C as the mercury returns to its former position. The mercury in C is covered with a layer of oil to prevent carrying harmful vapor into the room.

If the diffusion pump is heated electrically, the arm BGB is mounted horizontally (in place of BCB) so that



the mercury covers the bottom of G and is part of the circuit. When the water supply fails and A falls, the mercury runs to the left end of G and breaks the circuit. If the water supply is resumed, the circuit is reactivated when G reaches its horizontal position.

The device is somewhat sensitive to set up, but once the flow of water is correctly adjusted it provides trouble-free operation. As an additional precaution, the beaker F is mounted directly over the drain in case a sudden upsurge in water pressure causes overflow.

Work supported by National Science Foundation.

[1] Steel, C., Smith, R. F., and Summers, B., *J. Sci. Instr.*, **34**, 125 (1957).
[2] Houghton, G., *J. Sci. Instr.*, **33**, 199 (1956).
[3] Green, G. W., *J. Sci. Instr*, **35**, 147 (1958).
[4] Croft, A. J., *J. Sci. Instr.*, **25**, 386 (1948).
[5] Shur-flo, automatic interlock, Hays Mfg. Co., Erie, Penna.

Stanley Kirschner
Wayne State University
Detroit, Michigan

Adapting Machine-Sorted Punched Card Systems to Hand Sorting and Coding

Several foreign and American scientists, who have shown interest in the system of coding and abstracting chemical literature using IBM machine-sorted punched cards recently proposed by the author (*1*, *2*), have indicated certain reservations about adopting this system. The most serious is that it would prove of limited value, once adopted, if an individual moved to a location in which the necessary IBM equipment is practically unobtainable.

Consequently, the original machine-sorted punched card system has now been adapted for use as a hand-sorted as well as machine-sorted and coded system. In addition, the face of the IBM card on which additional abstract information about an article is written has been revised so as to simplify the coding procedure and to eliminate completely the preparation of the separate "program form" required by the previous system.

The previous card, IBM 894510 (*1*, *2*), provides guide lines for writing or typing the title and abstract information in addition to that which is punched into the card. If the writing or typing is done directly on the line, it will not be mutilated by the punched holes. The information which can be punched into the card is as follows: (a) the first two initials and the first eight letters of an author's surname, using the IBM letter code (*2*), (b) the original journal reference, using the four-letter "Coden" system devised by Bishop (*3*, *4*) for the abbreviation of journal names with the last two digits of the year, (c) the abstract reference, (d) the numbers of the reader's subject code representing those subjects with which the article deals, and (e) the atomic numbers of all the important elements in the article according to the method previously described (*1*). Space is also provided at the top of the card for interpretation into printed letters of the punched holes representing the author's name, journal reference, and abstract reference.

However, for this card, it is necessary that a separate program form (*1*) be used along with the card in order to provide the IBM key-punch operator with the necessary information to be punched into it. The reader fills out the separate program form and writes or types the title and a brief abstract on the IBM card as he reads the article.

The Revised Card

The revised card, IBM U20115 (Fig. 1), allows for the punching and interpreting of a card number (columns 65–68 plus a spare column 69) into each card in addition to the information which can be punched into the original card described above. The dotted lines are strategically placed so that additional abstract information and the title may be typed or written on the card without being mutilated by the punched holes. The lower part of the card itself comprises the program form for that card and the reader writes the information to be punched into the card in the appropriate spaces (which are spaced so that this writing or typing will not be mutilated), and the IBM key-punch operator punches the card from this information. The separate program form required with the previous card is thus eliminated, and the letters and numbers represented by all the punched holes in the card are always visible. The vertical dotted lines in columns 11–33 provide additional coding space above the atomic number set, should there not be sufficient room in these boxes to write all the atomic numbers of important elements mentioned in an article.

In addition to machine-coding and sorting (*1*, *2*), hand-coding and sorting of these cards with respect to subject numbers and/or date may be accomplished by maintaining a subject code book or chart. There should be as many pages in the subject code book as there are subjects in the reader's code (78 at present for this author)—one subject per page. Hand-coding requires that the number of every card which deals with a particular subject be recorded on the page devoted to that subject. Hand-sorting is accomplished by turning to a desired subject page in the code book and manually selecting those cards from the deck whose numbers are listed on that page. This assumes that the cards are kept in approximate numerical order. In addition, if a reader starts his deck with number 0001 and adds to it sequentially, his deck will also be arranged in approximate order of date of reading, which will sometimes facilitate sorting.

If hand-coding and sorting with respect to journal name or author are important, separate code books for these may also be maintained. A code book of the approximately fifty-six journals important to this author would list the card number of every card having a reference in a particular journal on the page in the book devoted to that journal.

Other advantages of these types of card systems for storing and retrieving information in the chemical literature have already been published. (*1*,*2*,*5–10*).

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(1) Kirschner, S., J. Chem. Educ., **34**, 403 (1957).
(2) Casey, R. S., Perry, J. W., Kent, A., and Berry, M., "Punched Cards," 2nd ed., Reinhold Publishing Corp., New York (1958), chap. 14 and others.

Presented before the Division of Chemical Literature, 137th Meeting of the ACS, Cleveland, Ohio, April, 1960.

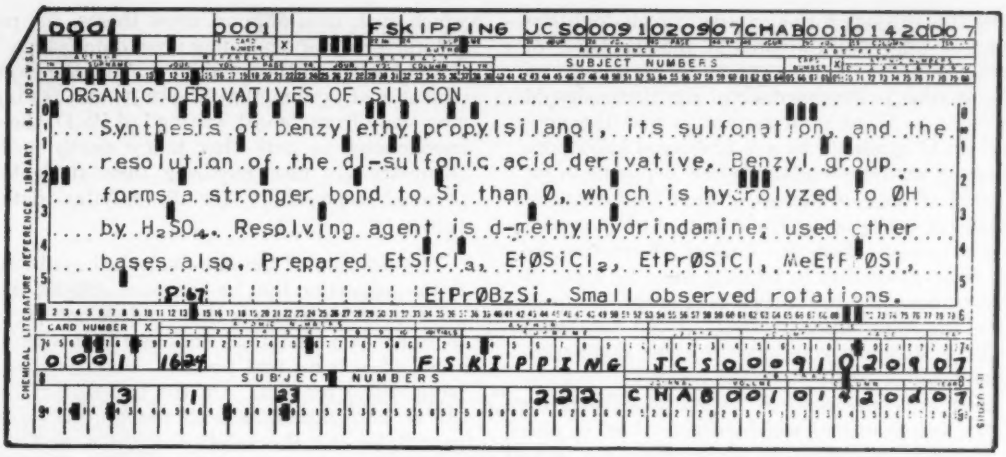
FSKIPPING JCS0009102090 7CHAB001014 2 0 0 7
SUBJECT NUMBERS
ORGANIC DERIVATIVES OF SILICON.
Synthesis of benzylethylpropylsilanol, its sulfonation, and the
resolution of the dl-sulfonic acid derivative. Benzyl group
forms a stronger bond to Si than Ø, which is hydrolyzed to ØH
by H2SO4. Resolving agent is d-methylhydrindamine; used other
bases also. Prepared EtSiCl3, EtØSiCl2, EtPrØSiCl, MeEtPrØSi,
P 67 EtPrØBzSi. Small observed rotations.
CARD NUMBER
0 0 0 1 1 1624
FSKIPPING JCS0009102090 7
SUBJECT NUMBERS
3 1 23 222 CHAB001014 2 0 0 7

Figure 1. A typical chemical literature reference library card (revised, 1960) with abstract, punched holes, and interpretation.

(3) Bishop, C., *Am. Documentation*, **4**, 54 (1953).
(4) Bishop, C., *Science*, **120**, 1038 (1954).
(5) Ames, S. R., and Kujawski, W. F., *Spec. Libr.*, **39**, 233 (1948).
(6) International Business Machines Corporation, "IBM Data Processing Machine Functions," IBM Corporation, New York, rev. ed., **1957**.
(7) Perry, J. W., and Kent, A., "Tools for Machine Literature Searching," Interscience Publishers, New York, **1958**.
(8) Berry, M. M., "Non-conventional Technical Information Systems in Current Use," National Science Foundation, Washington, D. C., **1958**.
(9) Anderson, I., *Ill. Libr.*, **31**, 405 (1949).
(10) Krieger, K. A., J. Chem. Educ., **26**, 163 (1949).

William MacNevin
The Ohio State University
Columbus

Analytical Chemistry and the Non-Analytical Graduate Student

A recent article[1] pointed out that Ph.D. students majoring in fields other than analytical chemistry are becoming progressively less informed and experienced in the analytical features of their thesis research, depending rather upon an analytical "service" for the analysis of products of their work. The response to this point from industry, universities, and research institutes has been such that it now seems appropriate to spell out in detail the need for more analytical chemistry in the education of all Ph.D. students as future research chemists.

The following are comments about the non-analytical Ph.D. made by directors of research:

"One of our greatest problems is with those members of our research staff, other than analytical, who have had so little analytical chemistry that they have little or no concept of the field."

"They have no idea of what a good analytical chemist can do for them and so a good portion of their effort is wasted."

"They cannot interpret or apply the analytical data given them."

"Instead of discussing the research problem with an analytical chemist, they take wrong samples at the wrong time and request some analysis . . . that gives them useless or erroneous results."

"Complex samples are marked 'Unknown' and further information is difficult to obtain from the research chemist on the theory that the less the analyst knows, the more accurate his analysis will be."

The present article is a plea for the inclusion of more analytical training and the development of better understanding of the use and value of analytical chemistry for the non-analytical Ph.D. student. Whether

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The many friends of Dr. MacNevin were greatly saddened by his sudden death in June of 1961. The manuscript for the article here presented was in process at the time.

Requests for reprints should be directed to Mr. James C. Bourke, Dept. of Chemistry, Ohio State University, Columbus, Ohio.

[1] MacNevin, W., J. Chem. Educ., **37**, 339 (1960).

he receives this through formal courses which doubtless could correct many of the present inadequacies, or through his advisor requiring him to be personally responsible for the analytical data of his thesis, is not too important. What is important is that the non-analytical Ph.D. graduate have a first-hand knowledge of the kinds of analytical methods now available in his research field, of their usefulness, of their limitations, of the methods of interpreting the results, and of equipment requirements. With this kind of information, he should develop astuteness in judging when an analysis will be worth doing: if the sample is of such quality as to provide the information desired; if the analytical result will be sufficiently unique to allow distinction from other possible products of the reaction; and the best or most practical method to select. There are many more such questions which reflect a kind of philosophy of analytical chemistry, as essential as is technique or facility in analysis.

Ability to recognize and answer such questions before an analysis is done, is only developed by a certain amount of actual experience. It begins in the undergraduate courses in analytical chemistry. But, just as the research chemist says that the only way to learn to do research is by doing it (one cannot depend upon reading alone to learn how), so one cannot develop a proper appreciation of analysis and its usefulness without doing a certain amount of it. For example, it is only rarely that the currently graduating Ph.D. in organic chemistry has ever done a carbon-hydrogen combustion analysis. As a result, his reaction to any compound he produces is to send it automatically for C-H analysis without sufficient concern for purity and probable significance of the results. This is not only expensive and wasteful of the analyst's time but reflects poor pedagogy in the university.

It is a too common practice in university research programs to allow graduate students to send unchecked samples to the analytical "service" without supervision. If the analysis agrees with the theory, this may be the end of the student's effort on this product; if it does not agree then he will purify it somewhat and return it for another analysis. An example is known of a graduate student sending in the same sample eight times to the analytical service with one intermediate crystallization each time until gradually changing analyses agreed with what was wanted. No further purification was attempted to see if a constant analysis had been obtained. Such procedure can hardly be called "scientific" and should not be tolerated as part of university educational practice.

At this point it should be realized that analytical service is only one among a group of services now expected by and provided for the graduate student. Included are glass-blowing, preparation of standard solution, translation, machine shop work, electrical repair, and care of special equipment. The danger is that the research chemist may be come helpless if these services are not provided. Excessive specialization during graduate study can easily become limitation.

It is to be deplored that many university programs do not require the nonanalytical graduate student to be responsible personally for the analytical data upon which his thesis is based. Considering the extent to which such data support most theses, the practice in the university of depending upon data from a "service" is a challenge to the reliability of the thesis and to the educational system that allows it, and is only a short step away from "ghost writing" of Ph.D. theses. It is encouraging to note that many *young* professors of chemistry are now requiring their students to take personal responsibility for all analytical data in their theses.

The reaction of the non-analytical graduate student to the suggestion that he be responsible for the analytical data of his thesis is that he does not have the time to do his own analytical work and that when he graduates and gets his first position, analytical services will be provided for him. On the question of time, there can be no compromise with the student's personal responsibility for the validity of the analytical data of his thesis. It means longer hours at the laboratory and much hard work; the student needs to learn that research for the Ph.D. degree is a serious business requiring the maximum in personal sacrifice for the sake of reliability of the conclusion. Universities have the responsibility for the development of this quality in their graduates when awarding their highest degree, the Ph.D.

The insidious reason is sometimes given that if the research conclusions of a student's thesis are eventually shown to be in error, the analyst can always be blamed. This reason is regarded facetiously by most graduate students but it has been used more than once when conclusions did not hold up.

The proposition that since industry provides analytical services, the student need not concern himself, is answered in part in the previous paragraph. But the argument by the graduate student, supported even by many of his professors, does not justify its validity within the educational pattern of a university. It also assumes that the graduate student will go into industry where services are provided, and not all do. If industry finds it to its best interest to provide such services as a kind of specialization of labor, there can be no quarrel with industry's decision to do it this way. But industry does reasonably expect that the Ph.D. hired as a research chemist will know the value of analysis to research and will have some basis for developing sound judgment in requesting analytical services.

Apart from the absence of the philosophy of analytical chemistry that could be developed during graduate study, the absence of ordinary undergraduate analytical knowledge is often apparent in the Ph.D. Prevailing recommendations to minimize or eliminate undergraduate analytical chemistry should now be looked at carefully as the first of the graduates of this system are beginning to appear in graduate school.

All Ph.D. students in whatever field of chemistry should have a critical conception of the value and usefulness of analysis in research in order to function satisfactorily as research scientists. Whether they obtain this in advanced courses or by being made personally responsible for obtaining the analytical data of their theses, obviously the need exists for them to make more intelligent use of analytical chemistry in research. The place to learn should be the university.

. . . from the Committee on INSTITUTES AND CONFERENCES

W. T. LIPPINCOTT, Chairman

The Committee on Institutes and Conferences stimulates institutes, conferences, and symposia in four areas: (1) improving the subject matter competence of teachers; 2) curriculum examination and development; (3) articulation between secondary school and college teachers, and between industry and education; (4) examining productivity in colleges and universities.

This committee works closely with the Committee on the Teaching of Chemistry. Usually the two schedule a joint session at National Meetings.

The Committee's activities are so broad in scope that a series of subcommittees has proved to be the convenient form of operation:

Summer Institutes. Under its Chairman, D. B. Summers, (Alton, Ill., High School) this subcommittee is constantly making summer institutes more effective. Two problems receiving current consideration are: (1) stimulating more institutes for teachers who are in greatest need of refresher work; (2) making the chemistry courses taught at summer institutes more directly applicable to the needs of the teacher without having the institute programs degenerate into presentations of merely a routine bag of tricks for the teacher.

Subject Matter Conference. Charged with stimulating one-to three-week conferences for college teachers on specific topics in chemistry, this subcommittee has catalyzed more than 20 such conferences during the past three years. Conference topics for 1961 include: Chemical Bonding, Nuclear Resonance, Non-Aqueous Solvents, Chromatography, Plant Biochemistry, and Colloids. Chairman R. K. Birdwhistell (Butler) hopes to initiate conferences on complex ion chemistry, organic reaction kinetics, electrochemistry, and other topics for the summer of 1962.

Negotiations are now underway to establish an annual series of two-week conferences on special topics in modern chemistry for college teachers and industrial chemists. Efforts are being made to get industrial, as well as NSF funds, for support.

The Undergraduate Curriculum. Generating conferences to examine and make recommendations for overhauling the undergraduate chemistry curriculum is the responsibility of B. R. Willeford (Bucknell) and F. H. Verhoek (Ohio State) and their subcommittee. The Bucknell Conference of 1960 grew out of activities of this group [see THIS JOURNAL, **38**, 251 (1961)]. Plans are proceeding for conferences in the summer of 1962 to continue this study.

Non-Majors' Chemistry Courses. At the Montana State Conference of 1960 [see THIS JOURNAL, **38**, 253 (1961)], a start was made on developing a modern, revitalized course for those students who take only a limited amount of chemistry. For the first time in recent years, scholars from sister sciences discussed in depth with chemists the ramifications and implications of this kind of course. All agreed that such courses are the very foundation of public understanding of science. Efforts to continue work in developing this program are progressing.

Undergraduate Laboratory Program. J. L. Hall (Colorado School of Mines) is Chairman of the group that is sampling current thinking regarding the undergraduate laboratory. Following this survey, plans call for a symposium at a National Meeting on new and novel approaches to undergraduate laboratory.

From its survey and the symposium this subcommittee hopes to have sufficient information to organize a conference to recommend improvements of current laboratory programs.

Industry-Education Relations. Working under the direction of D. S. Allen (Albany State Teachers College), this subcommittee is preparing a nationwide file of science councils and their activities. The file will be used to help establish better communication among the councils around the country, thus producing more effective industry-education cooperation on problems of science education.

In-Service Teacher Programs. This group is attempting to discover the greatest current needs of the in-service science teacher and to recommend types of conferences or symposia which the Committee should stimulate to bring these needs before individuals or groups who might be able to provide relief. E. T. Hofman (Notre Dame) is Chairman.

Evaluation Studies. The Wooster Conference of 1959 [see THIS JOURNAL, **36**, 533 (1959)] was set up to answer these questions: How do the very productive liberal arts colleges differ from the less productive colleges? What part does research play in the difference? Productivity was judged by the number of alumni receiving the Ph.D. in chemistry (including biochemistry) during the period 1936-1956. Results indicated that chemistry departments with a favorable research atmosphere are the most productive. For a variety of reasons, the Committee is interested in sponsoring a university evaluation conference similar to the Wooster Conference. Suggestions as to the best approach to this evaluation will be welcomed.

Chemistry Youth Corps. This subcommittee under Lyle Hamilton (Mobil Research Laboratories) will coordinate with the Committee on International Chemistry and with the Committee on College Teaching in helping set up international teaching projects. Dr. Hamilton's subcommittee is to explore ways of financing these projects.

Research Participation. The Research Participation Program of the NSF is one way that college teachers might initiate research programs. The committee is currently exploring ways of stimulating more college teachers to participate in such programs.

These subcommittees do not exhaust the possible future actions by the Committee on Institutes and Conferences. Other problems under study include coordination between junior college and college or university teachers; junior high and elementary science programs; effective coordination with corresponding committees in physics, mathematics, and biological societies.

Individuals interested in working with the Committee on Institutes and Conferences should contact the Committee Chairman.

Report of the New England Association of Chemistry Teachers

L. E. Strong
Earlham College
Richmond, Indiana
L. B. Clapp and **J. O. Edwards**
Brown University
Providence, Rhode Island

Geometry in the Beginning Chemistry Course

In the course of visiting high school classes in which the Chemical Bond Approach course is offered and college classes on the Visiting Scientist Program of the Division of Chemical Education, and in our own beginning chemistry classes, we have frequently been asked questions that seem best answered at this level by using structural considerations. In the discussion that follows the questions are stated as they have most often been asked and the answers are given as they are currently being answered in the CBA course although the discussion here is extended beyond this treatment in some cases. The answers are not the only answers nor the most sophisticated. They are the answers that might be given to a student in class at the time they are asked.

Pauling led the way in emphasizing the importance of structural concepts (for example, the radius ratio) in answering chemical problems. His book (*1*) recently revised, remains an excellent source for provoking questions and probing for answers to questions on structure. A classic case is Pauling's explanation of the acidities of oxyacids [for example, the series $HOClO_3$, $(HO)_2SO_2$, $(HO)_3PO$, $(HO)_4Si$] from structural considerations (*2*).

Why is the formula for carbonate ion CO_3^{-2} but silicate is $SiO_2(OH)_2^{-2}$; and nitrate, NO_3^-, while phosphate is PO_4^{-3}?

This question can be expanded to include other anions in groups IV and V as well as VI and VII as shown in Table 1. The simplest answer to the question is that the small atoms, carbon and nitrogen, are not large enough to accommodate four oxygens *in strong bonds*. If σ bonds can be considered to be formed by head-on overlap of p orbitals then π bonds in such cases may be thought of as arising from sidewise overlap of p orbitals after a σ bond is formed. Sidewise overlap in a π bond occurs in carbonate ion when three atoms are joined to carbon by σ bonds. The π bond between carbon and three oxygens gives stronger bonding than head-on overlap in four σ bonds with four oxygens. Small atoms of the second period tend to form double bonded (one σ and one π) structures, particularly with each other. Oxygen and other elements below it in group VI can form strong π bonds by sidewise overlap when a σ bond is also present whereas the halogens do not have this opportunity at comparable energy. The small size of the second period elements allows more complete sidewise overlap (π-bonding) since the σ bond is comparatively short.

In the larger third period atoms, this sidewise overlap is so imperfect as to allow only frail π bonding. The next element in each group is large enough to give good overlap for four σ bonds and the still larger atoms in the fifth and sixth periods form six bonds in an octahedral arrangement.

It is significant to suggest to beginning students that geometry (size and shape) plays an important role in determining the *formulas* of substances.

Size alone cannot be the full answer, however, for the difference between the second and third period elements, since carbon will form four sigma bonds with atoms much larger than oxygen (e.g., the lower halogens). Among the tetrahalides of carbon, a critical size for the halogen to give a stable compound is reached at bromine. Although carbon tetraiodide is a known substance, it decomposes easily at its own melting point and cannot be distilled. This suggests that the iodine atoms are crowded if not cramped in positions around the tetrahedral carbon.

Table 1. Formulas of Anions[a]

Period	IV	V	VI	VII
2	CO_3^{-2}	NO_3^-	...	...
3	$SiO_2(OH)_2^{-2}$	PO_4^{-3}	SO_4^{-2}	ClO_4^-
4	Ge[b]	AsO_4^{-3}	SeO_4^{-2}	...[c]
5	$Sn(OH)_6^{-2}$	$Sb(OH)_6^-$	$TeO_2(OH)_4^{-2}$	$IO_3(OH)_3^{-2}$

[a] The next element to the left of carbon in the second period, boron, is larger than carbon and can accommodate four groups. Borate ion, accordingly, should be written $B(OH)_4^-$ as has been demonstrated by Raman spectra and other evidence (*3*). The radius ratio of boron to oxygen can lead to a coordination number of four also.

[b] Germanate may have the same formula as silicate or it may be analogous to stannate. The formula is not presently known.

[c] The non-existence of perbromate ion is probably not a matter of geometry. It may be a matter of an excessively high oxidation potential. Potentials in periods 2 and 4 are much higher than those in 3 and 5.

This work was made possible in part by a National Science Foundation Faculty Fellowship held by one of us (L.B.C.) at Earlham College. He is also grateful to Brown University for a sabbatical leave during this time.

Presented before the NEACT at the College of the Holy Cross, Worcester, Massachusetts, May 14, 1960.

Why do carbon dioxide and silicon dioxide (silica) bear such a contrast in properties?

The sharp difference in melting point (1700°C for white sand or quartz and −77° subl. for dry ice) is generally the specific contrast that is implied. If the molecular formula for silica is written more correctly, $(SiO_2)n$, most of the difficulty in understanding in removed, for probably every grain of sand is just one molecule. The bonding is of the same type (predominantly covalent) but the individual bonds are different (Table 2). Each silicon is surrounded by four oxygens in a giant tetrahedral lattice similar to the diamond structure. Indeed, the high melting point suggests a closer resemblance between diamond and silica than between silica and carbon dioxide.

Table 2. Properties of Carbon Dioxide and Silica

	CO_2	$(SiO_2)n$
Melting point (°C)	−77 sub.	1700
Covalent radius (central atom)	0.67 Å	1.17 Å
Structure	Linear	Giant molecule with silicon tetrahedral
Bonding	$2\,sp + 2\,\pi$	$4\,sp^3$

Although the bond type in silica is called covalent, the difference in electronegativity of silicon and carbon will undoubtedly mean that the bonding in silica has more ionic character than the bonding in carbon dioxide.

The reason silicon does not (while carbon does) form π bonds readily was given in answer to the first question above; thus, it is not surprising to find four σ bonds for silicon in silica. In CO_2, the strength of the two sp and two π bonds is greater than that of four sigma bonds.

Why do two neutral molecules, H_2O and HCl, react to give two charged particles, H_3O^+ and Cl^-?

The energy relationships involved in this reaction bear out the statement of fact implied in the question but do not give an understanding of the event. A better picture can be drawn from structures and conditions of surface areas in the species involved.

$$\underset{\substack{\text{Base}_1\\ \text{V-shape}}}{H_2O} + \underset{\substack{\text{Acid}_2\\ \text{Linear}}}{HCl} \underset{<1\%}{\overset{>99\%}{\rightleftharpoons}} \underset{\substack{\text{Acid}_1\\ \text{Triangular pyramid}}}{H_3O^+} + \underset{\substack{\text{Base}_2\\ \text{Sphere}}}{Cl^-}$$

Since H is small in comparison with the other atoms involved we may look at the sizes of O, Cl, and Cl^-. The water molecule has a covalent radius near 0.67Å (oxygen), the HCl molecule near 1.28 Å, but the chloride ion has a radius of 1.81 Å. The important species to consider are the two bases. The ratio of surface area in H_2O and Cl^- is near 1:7.4 if the ratio of radii is 1:2.7. Water is a polar molecule and the oxygen carries some fraction of two negative charges. Parts of the surface of the small oxygen atom away from the hydrogens will therefore have a higher charge per unit area (charge density) than the ionic chloride bearing a total charge of −1. The polar oxygen in water is therefore able to offer more attraction per unit area for the proton than Cl^- does; water is the stronger base.

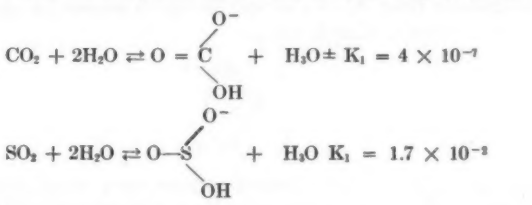
For a complete picture of this reaction, other factors such as energy of hydration of ions and concentration effect on base strengths of water and chloride ion would have to be considered, but the size and shape of the species involved give a clear picture of why the reaction starts.

Why does sulfur dioxide react more readily with water than with carbon dioxide? Why is sulfurous acid a stronger acid than carbonic acid?

Lewis structures for sulfur dioxide and carbon dioxide indicate one difference in the electronic structures of the two molecules. All electron pairs on carbon are shared, but one pair on sulfur is not shared. From considerations of electrostatic repulsion (*4*), carbon dioxide should be linear and sulfur dioxide a V-shape molecule. The angle in sulfur dioxide is 124° (*5*).

In terms of orbital pictures, carbon in carbon dioxide is described as carrying two sp hybrid (linear) bonds (σ bonds) and two π bonds; sulfur in sulfur dioxide is joined to oxygen in two (or three) sp^2 hybrid bonds; the bonds to oxygen are imperfectly described as two σ and one π bond. The angle (124°) is compatible with this bonding; the expected angle in sp^2 hybridization is 120°.

Considerable reorganization of bonds in linear carbon dioxide molecules is necessary to change to the planar hydrogen carbonate ion (sp^2 bonding) without accompanying bond improvement (lower free energy). Little energy is required to make the change in bonding in sulfur dioxide, but considerable bond improvement



obtains by the formation of one new σ bond to the third oxygen at the expense of the weak π bond. Actually there is some hybridization of the lone pair on sulfur (Lewis structure) in $\overline{O}SO_2H$ to give sulfur some sp^3 character. The ion will be pyramidal though not a regular tetrahedron. Even so, little reorganization is involved in the reaction to go from SO_2 to $\overline{O}SO_2H$.

The experimental facts are that carbonic acid, H_2CO_3, is slow to be formed from CO_2 and that the equilibrium amount in hydrated form is quite small (*6*). Both of

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$

the facts are consistent with bond formation involving considerable reorganization with little bond improvement. In the case of sulfur dioxide, where reorganization is less serious and where there is significant bond improvement, hydration appears to be rapid and to go to high yield.

The bonding in the two pure acids (carbonic, H_2CO_3 and sulfurous, H_2SO_3) should be quite similar, for the electronegativities of carbon and sulfur are the same. The K_1 values given above differ by a factor of 50,000. However, the difference in acid strength of carbonic and sulfurous acids is not correctly revealed by these apparent ionization constants. The constants given are for the process

$$(XO_2 + H_2XO_3) \rightleftarrows HXO_3^- + H^+$$

wherein the hydrated (H_2XO_3) and unhydrated (XO_2) forms are lumped together as "stoichiometric acid."

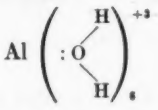
If one corrects for fraction present in unhydrated form for the case of carbonic acid, the ionization constant is 2.5×10^{-4}. Since most of the "stoichiometric acid" in the sulfur case is in the hydrated form, the correction here is negligible and the ionization constant is roughly the same as the value given. Thus the ionization constants of the two acids are less divergent from each other than they appear at first sight and the corrected values agree within the usual range of error for the rules of Pauling (*2*).

Why do the acidities of $Na(H_2O)_6^{+}$, $Mg(H_2O)_6^{+2}$, and $Al(H_2O)_6^{+3}$ increase in that order?

The relative size of the central atom of the hydrated ion supplies the answer to this question. For simplicity only one water molecule is considered around the central atom, but relative distances are the important consideration. If the ionic radius (crystal radius) is taken for the central atom and some constant radius for the oxygen in water (0.67 Å, covalent to 1.40 Å, ionic), then it is apparent that the bond length (size of the hydrated species) decreases sharply to the right.

$$\underset{\text{Na—O } (0.95 + r_{H_2O})}{\text{Na—O } (0.95 + r_{H_2O})};\ \underset{\text{Mg—O } (0.65 + r_{H_2O})}{\text{Mg—O } (0.65 + r_{H_2O})};\ \underset{\text{Al—O}(0.50 + r_{H_2O})}{\text{Al—O}(0.50 + r_{H_2O})}$$

At the same time the charge on the central atom increases sharply to the right. Since the distance Na—O is greater than Al—O, it will be much easier for positively charged aluminum in



to lose a positively charged proton to a weak base, water. The bond between sodium and oxygen will be too weak to have such an influence. Therefore $Al(H_2O)_6^{+3}$ hydrolyzes more completely than $Mg(H_2O)_6^{+2}$, and $Na(H_2O)_6^{+}$ scarcely reacts with water at all.

$$Al(H_2O)_6^{+3} + H_2O \rightleftharpoons Al(H_2O)_5OH^{+2} + H_3O^{+}$$
$$Mg(H_2O)_6^{+2} + H_2O \rightleftharpoons Mg(H_2O)_5OH^{+} + H_3O^{+}$$
$$Na(H_2O)_6^{+} + H_2O \rightarrow \text{n.r.}$$

Although the explanation based on size here is complicated by charge changes, one can give cases wherein this complication does not enter. The acidities of the hydrated alkaline earth ions decrease as the radius of the central ion increases from Be to Mg to Ca, etc. An exceptionally clear case is the hydrolysis of the lanthanides; as the size of the cation (in this closely similar set of ions) decreases, the tendency to hydrolyze increases.

How may we account for the properties of the series CH_4, NH_3, H_2O, HF, Ne?

An examination of nuclear and molecular structures (Table 3) is instructive. The total structures of these five substances in one sense differ only in the number of neutrons in the nucleus, for the total number of electrons and protons is 10. In methane, 6 protons are inside the central nucleus and 4 outside; in ammonia, 7 inside and 3 outside; in water, 8 inside and 2 outside; in hydrogen fluoride, 9 inside, 1 outside; in neon, all 10 protons inside. The number of neutrons increases from 6 to 10.

The two symmetrical molecules, methane and neon, are inert and differ sharply in chemical properties from the other three compounds. In at least two physical properties these two also differ sharply from the others in having low boiling points and melting points. The boiling points of related substances are most easily correlated with the surface area of the molecules (*7*). Although this empirical generalization has not yet been extended to unrelated molecules, perhaps inert molecules of this type could be considered. In any case, the larger molecule (CH_4) does boil higher than neon. The physical basis for this surface area to boiling point correlation presumably lies in the molecular polarizabilities, for volumes are proportional to polarizabilities as are the van der Waals forces. The surface area, then, is not the fundamental property that governs boiling point even though the correlations are better on this basis than in any other empirical relationship so far discovered.

The most important features of the other three molecules are their dissymmetries and the large electronegativities [Pauling scale (*8*)] of the central atoms N, 3.1; O, 3.5; and F, 4.1. Hydrogen bonding is therefore important in these molecules and their apparent molecular weights may be considerably greater than the formula weights. Electronegativities suggest that HF should form the strongest hydrogen bonds. It does, but this is not reflected in the boiling points where water falls out of line. One more structural feature needs attention in this unique molecule, water. The oxygen bears two sites in the octet occupied by hydrogen atoms and the same number of unoccupied sites (unshared pairs), while nitrogen and fluorine have unequal numbers of occupied and unoccupied sites. Hydrogen bonding can only result in two-dimensional polymers in the case of ammonia and hydrogen fluoride, but three-dimensional aggregates are possible in water. This is reflected in both the liquid (high bp) and solid states (high mp). A plot of melting point or boiling point of the five isosteres in Table 3 in the order given shows a decided peak for water (two possible hydrogen bonds per molecule) and intermediate points for ammonia and hydrogen fluoride (one possible hydrogen bond per molecule) with methane and neon at the low points (no hydrogen bonds possible).

Table 3. Structures of Five Isosteres

	Structure in nucleus: Protons	Structure in nucleus: Neutrons	Outside the central nucleus: Protons	Outside the central nucleus: Electrons	Melting point (°C)	Boiling point (°C)
	6	6	4	10	−184	−161
	7	7	3	10	−77	−33
	8	8	2	10	0	100
	9	10	1	10	−92	19
	10	10	0	10	−249	−246

Why is silicon tetrachloride so reactive in comparison with carbon tetrachloride?

The argument on relating structural symmetry and

physical properties (question 6) in molecules cannot be extended to chemical properties where the dissimilarity of the atoms that form the individual bonds governs the chemical properties.

Bonding in CCl_4, $SiCl_4$, $GeCl_4$, and $SnCl_4$ is of the same type, sp^3, but the electronegativity differences of the two atoms forming the bonds are presumably very marked (Table 4) even though the dipole moments of these symmetrical molecules are zero. The C—Cl bond is not strongly polar in comparison with the Si—Cl bond and in spite of molecular symmetry, the Si—Cl bond itself is easily distorted (polarized) and the molecule decomposes rapidly in hydrolysis, alcoholysis, and ammonolysis reactions (*9*). One other important factor is the availability of *d*-orbitals to Si, Ge, and Sn which are denied to carbon, at least at low temperatures. The tetrahedral silicon may first add water, for example, to give an octahedral d^2sp^3 structure before any Si—Cl bonds are broken.

The unsymmetrical covalent halides in groups V and VI reflect their strong polar character in boiling points (compare $SnCl_4$, $SbCl_3$, and $TeCl_2$ for example) and dipole moments. Presumably the V-shaped molecules in group VI would have dipole moments significantly different from zero.

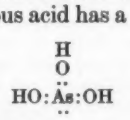
Table 4. Properties of Some Covalent Halides

	Formula weight	Boiling point (°C)	Electroneg. difference	Dipole moment
CCl_4	154	77	0.3	0
$SiCl_4$	170	57	1.1	0
$GeCl_4$	214	87	0.8	0
$SnCl_4$	261	114	1.1	0
PCl_3	137.5	74	0.7	0.8
$AsCl_3$	181	130	0.6	2.1
$SbCl_3$	228	220	1.0	3.9
SCl_2	103	59	0.4	...
$SeCl_2$	150	...	0.3	...
$TeCl_2$	199	324	0.8	...

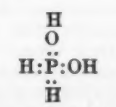
Why is the chemistry of phosphorus acid so different from that of arsenious acid?

It is known that phosphorous acid, H_3PO_3, is strong ($K_a = 5 \times 10^{-2}$) while arsenious acid is quite weak ($K_a = 6 \times 10^{-10}$). Such a large difference would not be expected from the normal family relationship. Also, it is known that the arsenic compound is often rapidly oxidized whereas oxidations of the phosphorus compound are invariably slow.

The difference between these two compounds is one of geometry. Arsenious acid has a structure



which is similar to other related oxyacids. It has an ionization constant consistent with the Pauling (*2*) rules, and the ease of oxidation presumably stems from the unprotected nature of the spare pair of electrons on arsenic. Phosphorous acid, on the other hand, has the structure



which is quite unusual. The third hydrogen is bonded to the phosphorus directly, so that only two O–H bonds are present. The ionization constant is consistent with the prediction of Pauling's rules for this structure. One can also explain the slow rates; there is no unprotected electron pair on phosphorus so that oxidation can only occur by breaking a phosphorus-to-hydrogen bond.

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Chem Ed

LETTERS

To the Editor:

I call attention of your readers to a simple method for the laying out of sites for bonds on spherical atoms. One simply draws a circle of the same size as the atom and lays out the desired angle with a protractor from the center of the circle. The desired distance is picked up with a compass or dividers from the points of intersection of the angle with the circumference and transferred to the ball. In case one has no dividers, pinholes in a strip of any flexible material will suffice to transfer distances. The most frequently encountered angles are 90°, 109° 28′, 120°, and 180°, or small distortions of these. For the more obtuse angles it is easier to transfer distances if the divider points are bent or if flexible strips are used. This method is somewhat different from that given by Mrs. Katherine Hoffman, this Journal, **37**, 637 (1960).

Wilbur L. Baker

Jacksonville University
Jacksonville, Florida

Chem Ed

BOOK REVIEWS

General Organic Chemistry

William C. Stickler, University of Denver, Colorado. Longmans, Green & Co., Inc., New York, 1960. x + 630 pp. Figs. and tables. 16 × 23 cm. $7.

In the words of the author, this text is "designed to give a general introduction to the field of organic chemistry." The book is planned for use in a full year course for premedical and other preprofessional students, and for chemistry majors; but, its organization is such that it also lends itself to adaptation for use in the concentrated one semester course.

The selection of topics for the discussions and the organization of the subject material reflect well the author's view expressed in the preface that "undergraduate texts must be brought into line with the newer concepts in theory and practice" and also indicate his understanding and appreciation of the difficulties usually experienced by the average student at the beginning of his study of organic chemistry.

Part I presents a gradual introduction of theoretical interpretations. The order is conventional, starting with hydrocarbons. In this section and throughout the text, the chemistry of aliphatic and aromatic compounds is treated concurrently rather than separately in two divisions. The fairly extensive treatment of stereoisomerism in Chapter 10 is fully justified by the over-all importance of this topic in organic chemistry today. To aid the student in his study, a list of new concepts, terms, symbols, and reactions introduced in the chapter, is found at the end of each chapter in this part, while in Parts II and III this enumeration is replaced by a list of well selected references. Study questions follow all chapters in the book. These questions are so formulated as to recall facts and to promote thinking.

Part II, by far the most extensive section of the book (312 pages), is divided into ten chapters. Here discussions are based on modern theoretical interpretations with emphasis on reaction mechanisms, and the student is called upon to use many of the concepts met first in earlier chapters. The physico-chemical aspects of compounds, their preparation and reactions are presented. The organometallic compounds are discussed in Chapter 16 where the magnesium, sodium, lithium, and arsenic derivatives are covered. While the π-bonded organometallic compounds are not included in this chapter, the preparation and properties of ferrocene are taken up in the chapter on heterocyclics.

The final three chapters in Part III introduce "several classes of naturally occurring substances which play indispensable roles in the chemistry of living organisms." The topics covered are: Amino Acids and Proteins, Carbohydrates, and Heterocyclic Compounds.

This carefully prepared up-to-date exposition of the principles of organic chemistry, written in a clear, definite, and interesting style should fill the needs of many college teachers for a satisfactory text for a one year undergraduate course in organic chemistry.

NAN V. THORNTON
Randolph-Macon Woman's College
Lynchburg, Virginia

Reviewed in This Issue

William C. Stickler, General Organic Chemistry
Paul H. Egli, Editor, Thermoelectricity
A. A. Frost and *R. G. Pearson*, Kinetics and Mechanism
Wendell M. Stanley and *Evans G. Valens*, Viruses and the Nature of Life
James W. Perry, Scientific Russian
Engelbert Broda, Radioactive Isotopes in Biochemistry
G. Burrows, Molecular Distillation
Joseph Hilsenrath, et al., Tables of Thermodynamic and Transport Properties of Air, Argon, Carbon Dioxide, Carbon Monoxide, Hydrogen, Nitrogen, Oxygen and Steam
Cecil L. Wilson and *David W. Wilson*, Comprehensive Analytical Chemistry. Volume 1B, Classical Analysis
Stella Goostray and *J. Rae Schwenck*, A Textbook of Chemistry
R. C. Vickery, Analytical Chemistry of the Rare Earths
P. C. Stevenson and *W. E. Nervik*, The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium
W. G. Wyckoff, Crystal Structures. Supplement 5

Thermoelectricity

Edited by *Paul H. Egli*, U. S. Naval Research Laboratory, Washington, D.C. John Wiley & Sons, Inc., New York, 1960. x + 407 pp. Figs. and tables. 15.5 × 23.5 cm. $10.

This book consists of 23 papers on various aspects of thermoelectric phenomena. Many of these papers were given at the Conference on Thermoelectricity sponsored by the Naval Research Laboratory in Washington, D. C., September, 1958. The preface by Egli is dated July, 1960, and the papers are of such a basic nature that they are still of current interest.

The translation of A. F. Joffe's books on thermoelectricity in 1957 has had an extraordinary catalytic effect on American publications in the field. A number of review articles on thermoelectric properties of semiconductors and several books devoted exclusively to thermoelectricity have already appeared.

In many respects the book under review is the best of the lot. In common with the Kaye and Welsh book (Direct Conversion of Heat to Electricity, Wiley, 1960), this is an edited compilation of conference papers by recognized authorities in the field with the resulting variations in writing. In spite of the variation of individual style and interest, the field is very well covered and the editor has done a good job of organization.

The book is divided into four sections: Fundamental Concepts in Thermoelectricity, Basic Parameters in Thermoelectricity, Chemical and Physical Properties of Materials at High Temperatures, and Measurement of Materials Properties. There is a conclusion section on Criteria for Materials Development. Each section is prefaced with a unifying summary by the editor. Individual papers range from reviews to original research.

There are many things about this book which appealed to the reviewer: (1) This book has a flavor of fundamental research (as opposed to an engineering approach). (2) The emphasis in most of the contributions has been on the significance of the experimental data collected to date, rather than on a detailed exposition of a particular experiment. Only in contributions on the thermal conductivity of germanium and indium antimonide were detailed results of a particular experiment presented, and in the latter paper (by Bettman and Schneider) considerable attention was paid to fundamental problems in the measurement of thermal conductivity. (3) The discussions are mostly nonmathematical and will have considerable appeal to a beginner in the field. One doesn't get bogged down by discussions of transport equations or with calculations of generator efficiencies. This simplification of the content material is effective in making the phenomena of thermoelectricity more familiar and much more understandable. As a result of this treatment the book has considerable heuristic appeal. (4) The book is an excellent compendium of the diverse factors which influence thermoelectric parameters and the influence of these factors on thermoelectric parameters is clearly stated.

Thermoelectricity is truly a "melting pot" science and has borrowed extensively from the techniques and results of more conventional disciplines. The chemist, physicist, and metallurgist all play roles in thermoelectricity but the individual may not be aware of the contributions and problems in the other fields. There is always a need for a book like this which correlates scattered information and relates it to the central problem.

The book should do much to spur increased research in the thermoelectric properties of materials and is highly recommended as a reference. It should be read by anyone interested in this new field who is looking for problems to investigate.

RICHARD C. CARLSTON
Grumman Aircraft Engineering Corporation
Bethpage, L. I., N. Y.

Kinetics and Mechanism

A. A. Frost and *R. G. Pearson*, both of Northwestern University, Evanston, Illinois. 2nd ed. John Wiley & Sons, Inc., New York, 1961. ix + 405 pp. Figs. and tables. 16 × 23.5 cm. $11.

The revisions in this second edition are largely due to Dr. Pearson and are chiefly in the areas of elementary reactions in the gaseous phase and in the study of very rapid chemical reactions. The extra material adds 62 pages to the first edition.

The authors are especially concerned with the study of the mechanisms of chemical reactions. In each case they go as far as they can in establishing just what elementary processes are involved and the nature of the corresponding activated complex. The book is carefully written and, while not exhaustive, includes many illustrative examples. It is well suited to graduate courses in chemical kinetics of intermediate scope. The modern statistical mechanics approach is developed and discussed; the authors provide a useful point of departure in this important field.

HENRY EYRING
University of Utah
Salt Lake City

Viruses and the Nature of Life

Wendell M. Stanley, University of California, Berkeley, and *Evans G. Valens*. E. P. Dutton & Co., Inc., New York, 1961. 224 pp. Illustrated. 17 × 24.5 cm. $4.95.

This book is an excellent elementary introduction to some fundamental aspects of biology today. It is an outgrowth of a series of eight half-hour films which were broadcast on an educational television station in San Francisco, in cooperation with the University of California. The conversion of these broadcasts into the form of a book is, in my opinion, highly successful. Professor Stanley and Mr. Valens were primarily responsible for the television programs and the organization of the book, but there are valuable chapters by six of Stanley's associates in the Department of Virology of the University of California—R. C. Williams, G. S. Stent, A. B. Pardee, Harry Rubin, C. A. Knight, and H. L. Fraenkel-Conrat. The general presentation is clear and should be understandable and interesting to the educated layman.

The emphasis is naturally on viruses, as molecules, as organisms, and as disease producing agents. However, studies on viruses have furnished a large part of the great recent advances in biochemical genetics, and the discussion here is carried on in a broad biological perspective.

The numerous excellent photographs are carefully coordinated with the text. Occasionally the reader might wish for specific captions attached to the photographs, rather than having to read through the adjoining text in order to make the correlation.

Some of the chapters will be harder reading than others, for the laymen. For instance, the section on "The Virus as a Molecule" by R. C. Williams, although excellently presented, involves an elementary discussion of ultracentrifuge and x-ray diffraction data, and its implications will by their very nature be most understandable to readers who already have a fundamental background in physics and chemistry. This is largely true also of the discussions by Knight and by Fraenkel-Conrat on "The Chemicals of Life" which deal with some of the fundamental problems involved in unraveling the biochemical mechanism of inheritance, and the nucleic acid code which presumably determines the specificity of protein biosynthesis. In other parts of the book the reader is introduced to some of the great discoveries in modern biology, such as transduction, with highly suggestive remarks concerning their possible significance in disease. The relation of viruses to the causation of cancer is thoughtfully explored.

As is natural, there is a strong emphasis on the achievements of the Virology Department at the University of California, which is certainly one of the great centers for such work in the world today. Although work in many other places is referred to, the reader unfamiliar with the field may not fully realize from this book how broadly international the whole development of modern virology has been.

The authors are experts who are also enthusiasts about their subject, and they have striven to be clear and accurate as well as interesting. The book should serve as valuable supplementary reading for many students, in conjunction with fundamental courses in chemistry and biology. It should also appeal strongly to many general readers who are eager to learn something of the great advances that are taking place in the borderland between chemistry and biology today.

JOHN T. EDSALL
Harvard University
Cambridge, Massachusetts

Scientific Russian

James W. Perry, University of Arizona, Tucson. 2nd ed. Interscience Publishers, Inc., New York, 1961. xxvi + 565 pp. Tables. 16 × 23.5 cm. $9.50.

Widespread intensification of interest in the Russian language in the post-Sputnik era will increase the demand for this new edition of Professor Perry's guide to Russian scientific literature, but the merits of the presentation would well justify even greater interest.

A particularly helpful feature, given a strategic position early in the book, is a systematic discussion, illustrated with tabulated glossaries, of ways in which Russian terminology adapts borrowed technical terms to the language. These terms are often but not always obvious equivalents of the transliterated counterparts, and these aids to their detection are useful. More attention to the considerable Greek and Latin influence in native Slavic words would have been helpful to an earlier generation of English-speaking scientists, but so few now study Greek or Latin that this omission will scarcely be missed.

The attention given to pronunciation, grammar, and sentence structure is judiciously arranged to suit the declared purpose of aiding students to read, while leaving instruction in speaking Russian to other (preferably more personal) sources; it includes recognition of the aid to understanding often contributed by an approximate idea of the pronunciation of a word.

Transliteration, a thorny question when 32 letters must be compressed into 26, gives preference to the system employed by *Chemical Abstracts* but recognizes other systems too. Facility in translation is given an assist every now and then, often by way of polite but firm prodding toward smooth renderings and away from the common tendency to translate too literally. This calls for frequent references to idiomatic differences between the ways followed by equivalent English and Russian expressions. Fortunately for American students, Professor Perry is an American and anglicisms, though occasionally recognized, are not allowed to cloud the issues.

Reading exercises, taken from Russian literature and illumined by notes, are well selected for practice in reading and translation, and become more involved as the lessons progress. Translation exercises also progress toward more difficult selections. Abbreviations receive attention through the text and are discussed in a short appendix with glossary.

The new edition is an improvement over the first one of a decade ago, both as to text and as a bookmaking job. Binding, paper, typography, and accuracy are fully acceptable.

JULIAN F. SMITH
Lenoir-Rhyne College
Hickory, North Carolina

Radioactive Isotopes in Biochemistry

Engelbert Broda, University of Vienna, Austria. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1960. x + 376 pp. Figs. and tables. 15.5 × 23 cm. $11.50.

In view of the rapid expansion and significance of radioisotopic methods in biochemical research, it is necessary to acquaint both student and research worker with the principles of radioisotope applications to living and non-living biological systems and to review the most outstanding results of this new methodology. In an attempt to meet both requirements the author has produced a most valuable work that unites the features of a textbook with those of a review, but suffers unavoidable shortcomings which such a synthesis brings.

The chapters dealing with radioisotope methodology which comprise about one third of the volume are a good introduction, but do not supply adequate knowledge to biologists and biochemists who wish to apply these powerful but extremely intricate methods to their own research problems. The main part of the book, applications of these techniques to biochemical problems, is best characterized by the fact that 3380 pertinent references are critically evaluated along with quotations from 81 books and 108 collective volumes.

This very comprehensive synopsis of an enormously large field constitutes the main value of the present volume, but also requires concise and condensed treatment. It will be difficult reading for those who have no more knowledge of radioisotopes than the author offers in the introductory chapters or who do not have complete familiarity with the complex biochemical problems under discussion.

There are unsolved problems in radioisotope application *in vitro* and particularly *in vivo*. The author makes the generally accepted distinction between "radiochemistry" and "radiation chemistry" and then says that "within the compass of the book radioactive atoms will be used as labels only, and the radiation emitted by them will be used for their analytical detection only. Hence, in this book it will always be tacitly assumed that the rays produce no disturbing effects on the materials investigated." Is this assumption justified? Such effects have been definitely established with tritium which tends to induce polyploidism in plant cells. Whether radioisotopes of higher atomic weight such as C^{14}, P^{32}, or S^{35} can affect a sensitive nuclear emulsion, as in the case of autoradiography, without affecting the biological matter through which the emitted radiation must pass in much greater strength, only future research will tell. This limitation, however, should not exclude the use of radioisotopes as tracers in "bulk" metabolic studies and it is here where their greatest value lies and to which the author has devoted the largest space and greatest emphasis.

However, if we wish to elucidate in greater detail the intricacies of the metabolic mechanisms by way of radioisotopes, another limitation appears. This method is based on the assumption that radioatoms behave exactly as the corresponding stable atoms except for the emission of radiation and the admittedly small radioisotope effect. However, recent investigations on organic compounds tagged with radioisotopes have shown that radioactive atoms change their place within the molecule due to the development of electric charges, ionization, radical formation, and reconsititution, especially if the radioatom is held only by weak chemical bonds. More research in this field will be necessary before we can draw definite conclusions on the structure of the original or metabolic product from the place of the radio atom in the degradation or metabolic end product.

In spite of these limitations radioisotopes have become a powerful tool in biochemical research and it is, therefore, essential that chemists, biochemists, and biologists familiarize themselves with the fundamental principles of its application and the most outstanding results so far attained. To all of them the book is warmly recommended, although the concentration of an enormous amount of material in a slender volume makes for difficult reading. The conciseness of the presentation also posed a most difficult problem for the translator which he has solved satisfactorily.

FRANCIS JOSEPH WEISS
Science and Technology Division
Library of Congress
Washington, D. C.

Molecular Distillation

G. Burrows, Associated Electrical Industries, Ltd., Manchester, England. Oxford University Press, New York, 1960. viii + 214 pp. Figs. and tables. 14.5 × 22.5 cm. $5.50.

Although addressed to engineers by a professional engineer who has been associated with the development of the open-path still for 30 years, this book could well serve as a standard college text, particularly if the preface of background material were rewritten to interest the novice.

The teachers of physics and more advanced physical chemistry will find all calculations and formulae necessary to make the qualitative operation of laboratory stills quantitative. An example is the separation of a binary mixture in the batch still which is presented graphically as well as by the Rayleigh equation.

Chapter 1 deals with the gas laws as applied to evaporation per se and evaporation into an atmosphere of residual gas. Chapter 2 presents the Langmuir equation which connects the vapor pressure(s) with rate(s) of unobstructed path distillation and the various factors, grouped as the evaporation coefficient, which reduce the rate below the maximum calculated. Chapters 5 and 7 deal with apparatus—laboratory and industrial stills and designs that have aimed at making an automatically operating repetitive or fractionating still. Chapters 4 and 8 deal with supportive technology, the kinds of pumps and gauges required, how to degas raw feed material and calculate the anticipated quantity of gas to be removed, and how to design for gas removal.

The book is unique and as far as mathematical treatment is concerned, almost exhaustive. However, the reader (lecturer) wishing to present a rounded story to students, will want to consult Perry and Hecker, both in articles in Weissberger's "Techniques of Organic Chemistry, Vol. 3"; Howatt's review in "Chemical Age" and earlier reviews by Fawcett, Burrows, and associates in "Chemistry and Industry" and Hickman's article in "Chemical Reviews." If the teaching is to extend to chemical engineers, the finest source material is in the Search Room at the Patent Office, Department of Commerce, where in Class 202 can be found in a few packed folders the whole panorama of vacuum stills and vapor pumps from the turn of the century to the present, including the U. S. equivalents of Geoffrey Burrows' own English patents. Here, rather than in the textbooks, are the pictures and diagrams for lantern slides.

The molecular still was born in Sweden and Britain and it was C. R. Burch at Metropolitan Vickers who enunciated and applied the principles to organic chemistry. Much of the development has been done by Burrows in the Metropolitan-Vickers laboratory and it is appropriate that the first book should spring from this locale. If the treatment tends towards the anglocentric, this is regrettable only where other approaches fail to find space in just 200 pages. Two copies, please, of this book in each chemistry department, one for the library, one for the work bench.

KENNETH HICKMAN
Rochester, New York

Tables of Thermodynamic and Transport Properties of Air, Argon, Carbon Dioxide, Carbon Monoxide, Hydrogen, Nitrogen, Oxygen and Steam

Joseph Hilsenrath, et al., National Bureau of Standards, Washington D. C. Pergamon Press, Inc., New York, 1960. xiii + 478 pp. Figs. and tables. 20 × 26 cm. $20.

Perhaps the best way to review a book of this sort is merely to describe its contents without comment.

The tables include compressibility factors, densities, specific heats, enthalpies, entropies, specific heat ratios, sound velocities, viscosities, thermal conductivities, Prandtl numbers, vapor pressures, and coefficients for equations of state.

This material was originally published as National Bureau of Standards Circular 564 by the United States Department of Commerce. In its present form it is reprinted with revisions to 1960.

W. F. LUDER
Northeastern University
Boston, Massachusetts

(*Continued on page A766*)

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by ALAN F. CLIFFORD, *Purdue University*

Uses the relationships of qualitative analysis to teach the chemistry of the periodic table in a systematic fashion, showing how the analytical scheme is built on and reflects the systematics of the periodic table. Thus the "solubility rules" are expanded and shown to be examples of trends within the periodic table.

1961 515 pages Text list: $6.95

Organic Chemistry

by KEITH M. SEYMOUR, *Butler University*

Presents those facts and principles which serve to give students a working knowledge of the more important types of organic compounds. Pertinent theories and new concepts are used only after the experimental basis for them has been studied and when they contribute to the understanding of the material under consideration.

1961 321 pages Text list: $6.75

Experimental Nuclear Chemistry

by GREGORY R. CHOPPIN, *Florida State University*

Designed to help teach the techniques and necessary basic theory for utilization of radioisotopes in research and experimentation. A variety of experiments and techniques are included with a discussion of the theory behind each.

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by RAY Q. BREWSTER and WILLIAM E. MCEWEN, *University of Kansas*

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BOOK REVIEWS

Comprehensive Analytical Chemistry. Volume 1B, Classical Analysis

Cecil L. Wilson, Queen's University of Belfast, Ireland, and *David W. Wilson*, Sir John Cass College, London. Elsevier Publishing Co. Distributed in the United States by D. Van Nostrand Co., Inc., Princeton, New Jersey, 1960. xxii + 878 pp. Figs. and tables. 16.5 × 23 cm. $30.

This is the second part of Volume 1, Classical Analysis. As was part one (THIS JOURNAL, **37**, A 384 (1960)) this contribution to the literature of analytical chemistry was eagerly awaited. Superlatives are insufficient to describe the excellent scope and value of this new chemical series. The editors, their advisory board, and the contributors to each part are to be highly commended for their combined efforts.

Volume 1A, Classical Analysis, consists of six chapters including chapters on: Inorganic Qualitative Analysis, Organic Qualitative Analysis, and Inorganic Gravimetric Analysis. Volume 1B includes chapter 7, "Inorganic Titrimetric Analysis" (398 pages) and chapter 8, "Organic Quantitative Analysis" (429 pages). As in 1A there is good balance between the theoretical and practical aspects of the topics. The laboratory directions and accompanying notes for each analytical procedure are detailed and clear.

Chapter 7 is composed of 10 parts including passages on theory and principles, apparatus, acidimetry and alkalimetry, argentometric methods, 11 commonly used oxidants and reductants, a 98 page section devoted to titrations with EDTA, and a brief section on miscellaneous reagents. To illustrate the breadth of coverage presented in this chapter attention is drawn to the EDTA passage. Here are included such topics as stability of complexes, visual and instrumental end-point detection, list of elements determinable, procedures involving both direct and back titrations, and general statements on precautions and calculation of results.

Chapter 8 includes 4 basic subdivisions: Treatment and Weighing of Samples, Determination of Elements, Determination of Functional Groups, and Titrations in Non-aqueous Solvents. The elements covered are carbon, hydrogen, nitrogen, the halogens, sulfur, oxygen, and many metals. The analyses for all common functional groups are covered in detail. It is especially valuable to have this up-to-date compilation of these elemental and functional group methods. The passage on non-aqueous titrations is brief (59 pages), but the reference list for this passage is very extensive.

Figures and tables are adequate. A more adequate index could have been prepared.

It is difficult in a comprehensive text of this type for each reader to be in complete agreement with all aspects of the manner of presentation. Any criticisms, however, become minor when it is realized that these volumes are peerless. Volume 1B is a first class work containing more than 2000 references to the original literature. Enough said!

J. M. PAPPENHAGEN
Kenyon College
Gambier, Ohio

A Textbook of Chemistry

Stella Goostray, Philadelphia General Hospital, Philadelphia, Pennsylvania, and *J. Rae Schwenck*, Sacramento City College, Sacramento, California. 8th ed. The Macmillian Co., New York, 1961. xiii + 502 pp. Figs. and tables. 14.5 × 21.5 cm. $6.95.

This book is written for a one year course for nurses. The authors are extremely optimistic that student nurses may assimilate inorganic, organic, and biological chemistry in a single course. Especially is this true with the more difficult biochemistry based on a meager foundation of fundamental chemistry presented as a hodge-podge of facts with very few correlating principles. The concepts of the mole, periodic table, equilibrium, atomic structure, and molecular bonding are mentioned briefly but rarely used. The Arrhenius concept of acids and bases is used throughout. Electron transfer is not used with oxidation-reduction reactions.

Words and terms are used without definition, although a glossary is provided in the appendix. On page 23 atomic weight is used but not defined until page 35. Exponential numbers are used as early as page 34 with an inadequate explanation of such numbers on page 204.

(*Continued on page A768*)

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LABORATORY OPERATIONS IN ORGANIC CHEMISTRY

By W. B. Renfrow and P. J. Hawkins; both, Oberlin College

Techniques now common in modern research are included in this up-to-date manual—infrared and ultraviolet spectroscopy, correlation of structure and chemical reactivity by measurements of ionization constants and reaction rates, countercurrent distribution, gas chromatography, use of punched cards, and qualitative organic analysis. All experiments have been thoroughly tested under actual teaching conditions, and detailed discussions of their essential features are included. *Spring, 1962*

A TEXTBOOK OF INORGANIC CHEMISTRY

By S. Young Tyree, University of North Carolina, and Kerro Knox, Bell Telephone Laboratories, Inc.

1961, 434 pp., Ill., $7.00

Designed for introductory courses, this text provides a well-defined treatment of basic chemical behavior and the latest theoretical concepts in inorganic chemistry. Each group of elements, organized according to the periodic table, is analyzed with regard to occurrence and history, preparation and physical properties, as well as chemical properties and the uses of compounds.

LABORATORY PRACTICE OF ORGANIC CHEMISTRY, Fourth Edition

By G. Ross Robertson and Thomas Jacobs; both, University of California, Los Angeles

An extensive, but informal treatment of the basic principles of laboratory manipulations, including a detailed discussion of chemical literature and a special chapter devoted to the writing of a research report. Discussions of theories and general techniques have been thoroughly revised. Additions, deletions, and improvements in experiments have been made on the basis of reports from users of the third edition. *Spring, 1962*

SEMI-MICRO LABORATORY EXERCISES IN GENERAL CHEMISTRY, Third Edition

By J. Austin Burrows and Paul Arthur; both, Oklahoma State University; and Otto M. Smith, Kansas State Teachers College

Nine completely new experiments introduce students to a variety of topics not commonly included in general chemistry—radioisotopes, paper chromatography, determination of ionization constants, argentimetric titrations, and modern applications of ion exchange resins. All other experiments have been thoroughly revised and brought up to date, with additional quantitative experiments offering many opportunities to use the latest techniques and principles. *January, 1962*

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On pages 204-5, *p*H is defined in terms of logarithms, but logarithms are neither defined nor tabulated in the book. On page 217 there is a suggested difference between valence and undefined oxidation number, and this is the only time the latter term seems to appear in the book, including the glossary.

There are statements which vary from the fallacious to the half-true to the misleading. These are the kinds of statements which students will grasp and remember. The following are examples: "Acids, bases, and salts are ionic compounds . . ." (p. 172); "All bases in water solutions are alkalies but not all alkalies are bases" (p. 181); In discussing methods for expressing hydrogen ion concentration, "One is by use of the c*H* notation, which represents the number of grams of hydrogen that are actually ionized within a liter of solution" (p. 204).

For those familiar with the seventh edition, the format is similar. The new edition is more clearly divided into three parts: I. Basic Concepts of Chemistry (Chapters 1–12); II. The Chemistry of Carbon Compounds (Chapters 13–16); III. Applied Biological Chemistry (Chapters 17–29). As before, each chapter begins with a survey and outline and ends with a summary and questions and exercises. The entire book has been revised, but the text in Parts I and II is very similar to chapters 1–17 in edition seven, except that the old chapter 13 on the halogens and alkali metals has been condensed and incorporated into the new chapter 2.

The questions and exercises are mostly the same.

Part II has been most extensively revised and expanded from five to 13 chapters to give a more complete treatment to foods, enzymes, digestion, metabolism, vitamins, inorganic salts, hormones and blood. The appendices include a bibliography, glossary and a section on the removal of stains. The section on basic mathematics has been omitted in line with the almost complete omission of arithmetic.

If it is true, as the authors state, that more and more student nurses are coming with a background of high school chemistry, books of this type which are inferior to the modern high school texts in chemical background material, will certainly discourage more prospective nurses than they will encourage.

The chemistry course for nurses still awaits a modern, authoritative, and imaginative textbook.

MILTON K. SNYDER
The Colorado College
Colorado Springs, Colorado

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Analytical Chemistry of the Rare Earths

R. C. Vickery, Malibu, California. Pergamon Press, Inc., New York, 1961. Volume 3 of the International Series of Monographs on Analytical Chemistry. viii + 139 pp. Figs. and tables. 14.5 × 22 cm. $6.50.

The Radiochemistry of the Rare Earths, Scandium, Yttrium and Actinium

P. C. Stevenson and *W. E. Nervik*, both of the Lawrence Radiation Laboratory, University of California, Livermore. National Academy of Sciences, National Research Council, Nuclear Science Series, NAS-NS-3020, 1961. Available from the Office of Technical Services, Department of Commerce, Washington, D. C. x + 282 pp. Figs. and tables. 17 × 24 cm. Paperbound. $3.

The increased interest in the chemistry of the lanthanide elements is reflected in the simultaneous appearance of these two monographs. In the first, Dr. Vickery has provided a review of the different techniques used in rare earth analysis. Descriptions are given for sample decomposition, qualitative detection, separation procedures, and both instrumental and non-instrumental quantitative techniques. Perhaps the most valuable aspect is the critical evaluation throughout of the various procedures with precautions against the various pitfalls which can frustrate the uninitiated. In particular the chapters concerning absorption and emission spectrometry–visible, U.V., and X-ray–should be of interest to every chemist interested in instrumental analysis of the lanthanides. In general, the book is easy to read and well-referenced with only an occasional mistake (e.g., the omission of Table I in Chapter 3). Too descriptive and too limited in scope to be of broad general interest, this monograph should be of interest to students of analytical chemistry who desire to broaden

(*Continued on page A770*)

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☐ **PHYSICAL CHEMISTRY**

By GEORGE H. DUFFY, South Dakota State College, Available January, 1962.

This text has been prepared as an introduction to physical chemistry for students who have had calculus and have followed the modern chemical-bond approach in their introductory courses. The theoretical side of physical chemistry is emphasized and only enough descriptive and experimental material is presented to support the arguments and to form exercises in applying the theory.

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☐ **PRINCIPLES OF ORGANIC CHEMISTRY,** ***Third Edition***

By JAMES ENGLISH, and HAROLD CASSIDY, Yale University. 515 pages $8.95.

A general revision updating an established text. Primarily for full-year courses for pre-meds and other non-majors, it is also suitable for one-semester courses. Avoiding the encyclopedic approach, the authors present only topics necessary to demonstrate basic principles.

☐ **STEREOCHEMISTRY OF ORGANIC COMPOUNDS**

By ERNEST L. ELIEL, University of Notre Dame. McGraw-Hill Series in Advanced Chemistry. *Available February, 1962.*

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☐ **INTRODUCTION TO GENERAL INSTRUMENTATION**

By EDWARD J. BAIR, Indiana University. McGraw-Hill Series in Advanced Chemistry. *Available January, 1962.*

An introduction for the experimental chemist to a detailed understanding of the design and operation of chemical instruments. Emphasis is on the flow of signals and the information they represent. Designed for graduate students and research workers, the book covers a representative collection of topics which should give the student an insight into new advances in instrumentation as they appear in chemical literature, and an insight into the art of designing instruments for new applications.

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their horizon to include a group of elements likely to become increasingly important.

Dr. Vickery recants an earlier view that ion exchange techniques were of slight importance. However, he still fails to describe the full versatility of these techniques for the lanthanides, and gives few references to guide the reader to a more complete knowledge. A second criticism which can be made is the rather useless chapter on Radiochemical Techniques in which the discussion is quite inadequate and sometimes even misleading. However, these areas which constitute the two faults in an otherwise useful and well-written book are very adequately treated in the monograph by Drs. Stevenson and Nervik.

This second work is one of a series of monographs on the radiochemistry of the elements prepared under the sponsorship of the Subcommittee on Radiochemistry of the National Academy of Sciences–National Research Council. (See THIS JOURNAL, **37**, 386 (1960), **38**, 72 (1961).) The chemistry of the lanthanide elements is reviewed with emphasis on the complexes of these elements both with inorganic and organic ligands and on the results of the studies by solvent extraction and chromatographic techniques. A great body of information is presented with little attempt at critical evaluation. The latter part of the book is devoted to 29 separation procedures for these elements. Any reader of this monograph cannot help but be aware of the necessity for much more research on the lanthanides and for this reason it is recommended to all students of inorganic chemistry.

These two monographs complement each other very well. Neither discusses lanthanide chemistry from a fundamental viewpoint, both being descriptive in nature. As specialized monographs, they are of interest primarily to the chemist who occasionally encounters these elements. Their value to students is more limited although both suggest many experiments with these elements which could be included in inorganic and analytical laboratory courses. It is to be hoped that these volumes may provide the necessary stimulation for the production of a fundamental text on these elements.

GREGORY R. CHOPPIN
Florida State University
Tallahassee

Crystal Structures. Supplement 5

W. G. Wyckoff. Interscience Publishers, Inc. New York, 1960. 20 × 25 cm. $26.50.

The publication of supplement 5 completes this monumental work, the first portion of which was issued in 1948. Additions to Chapters 2–15 are included. Some are supplementary pages. Others are pages to replace those issued earlier. Inorganic Formula Index, Mineralogical Name Index, and Index to Organic Compounds are also provided in the present supplement. See THIS JOURNAL, **26**, 289 (1949), **35**, A620 (1958), and **36**, A533 (1959).

W.F.K.

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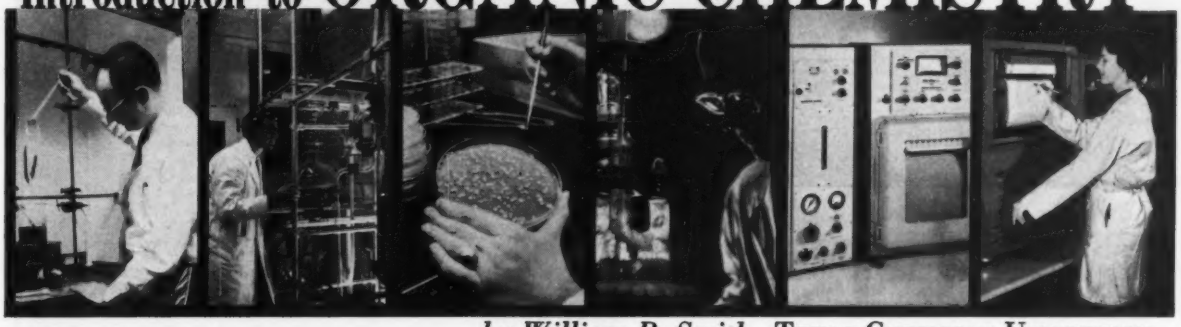

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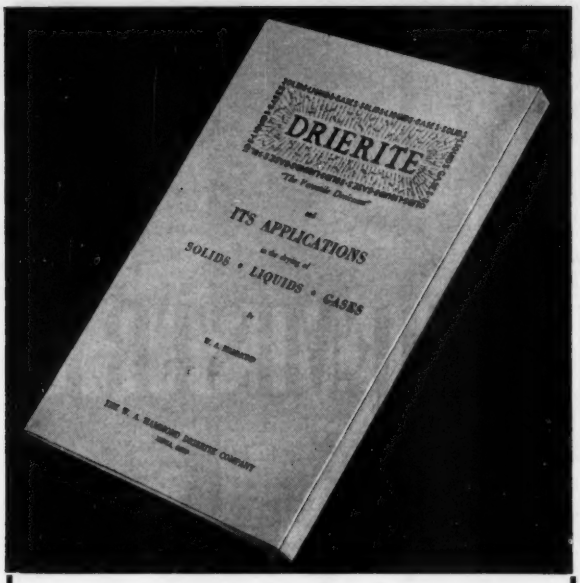

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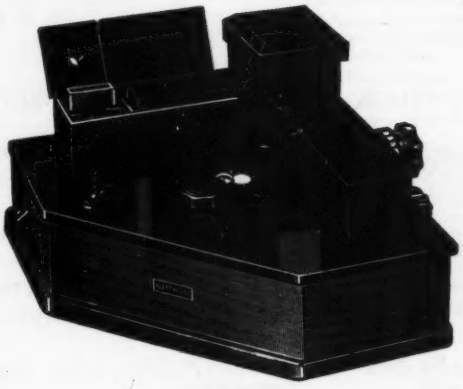

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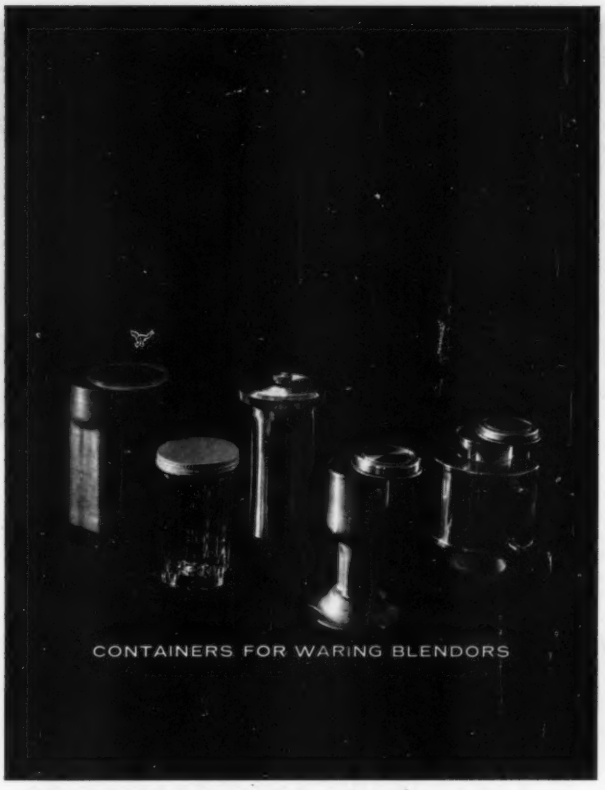

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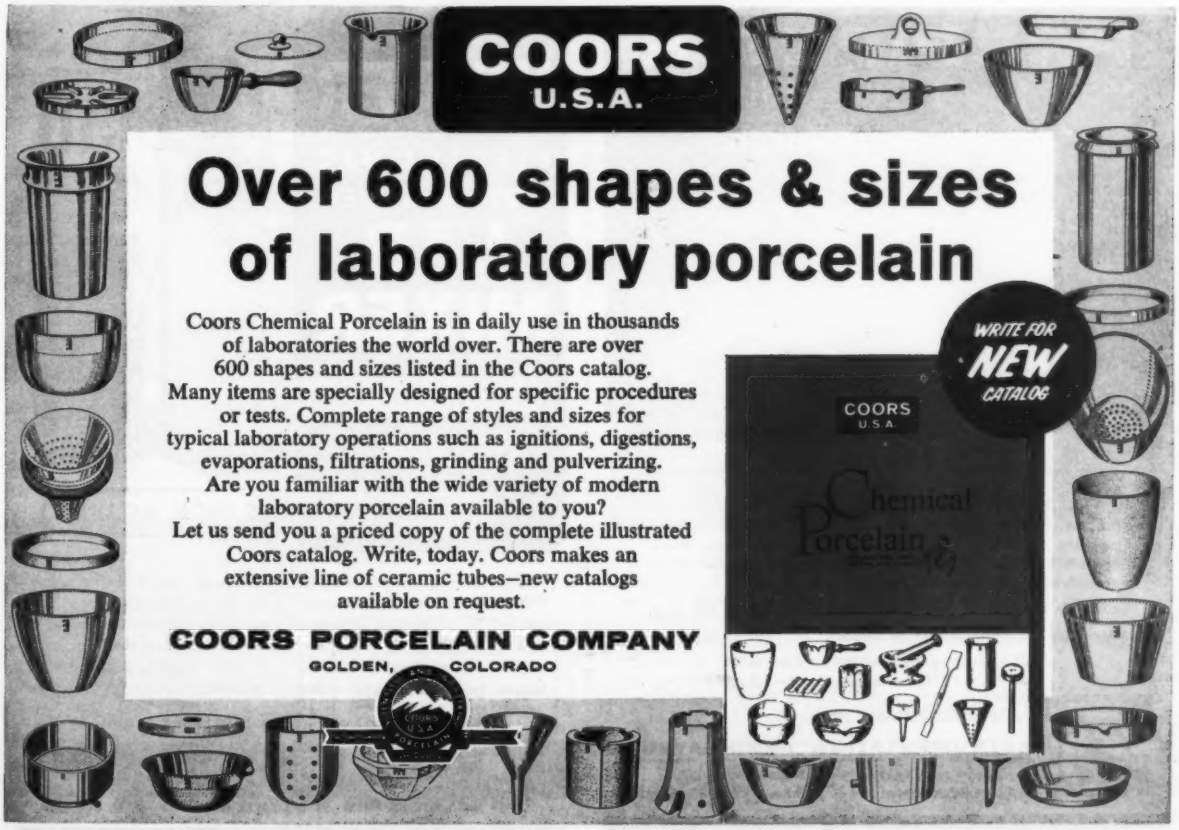
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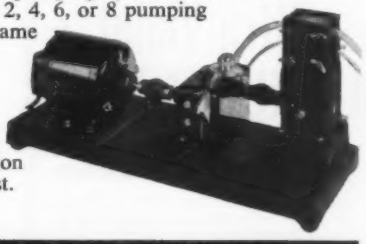

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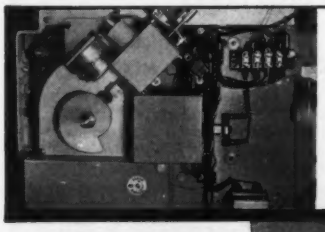

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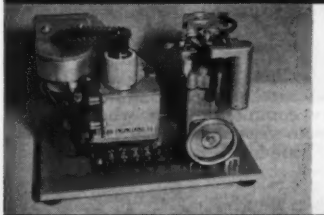

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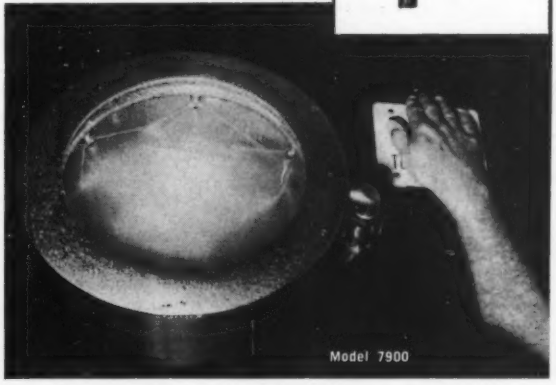

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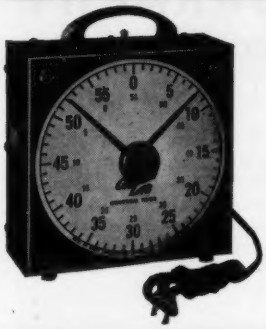

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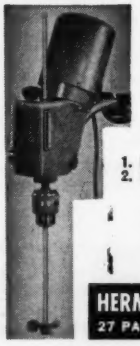

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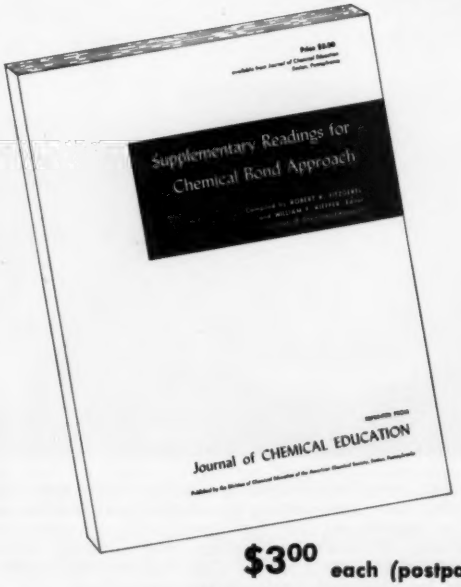

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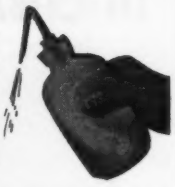

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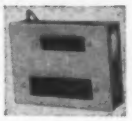

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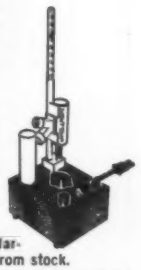

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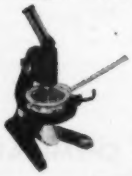

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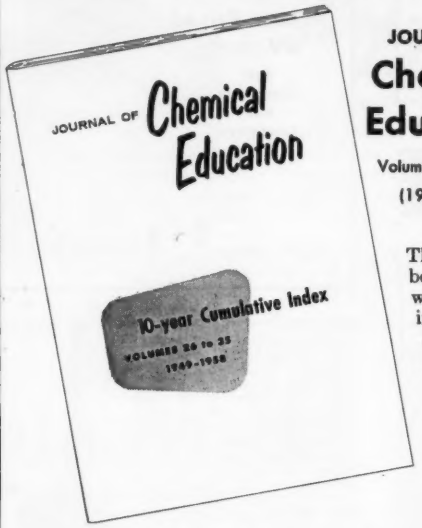

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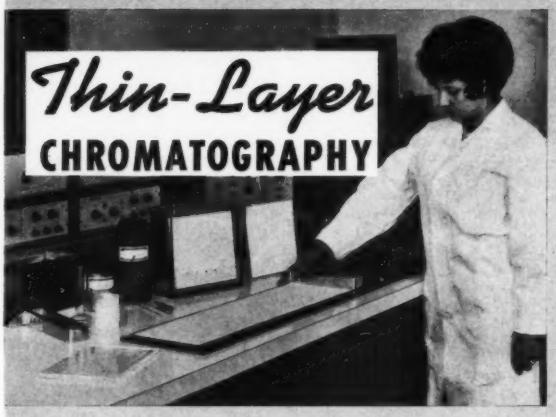

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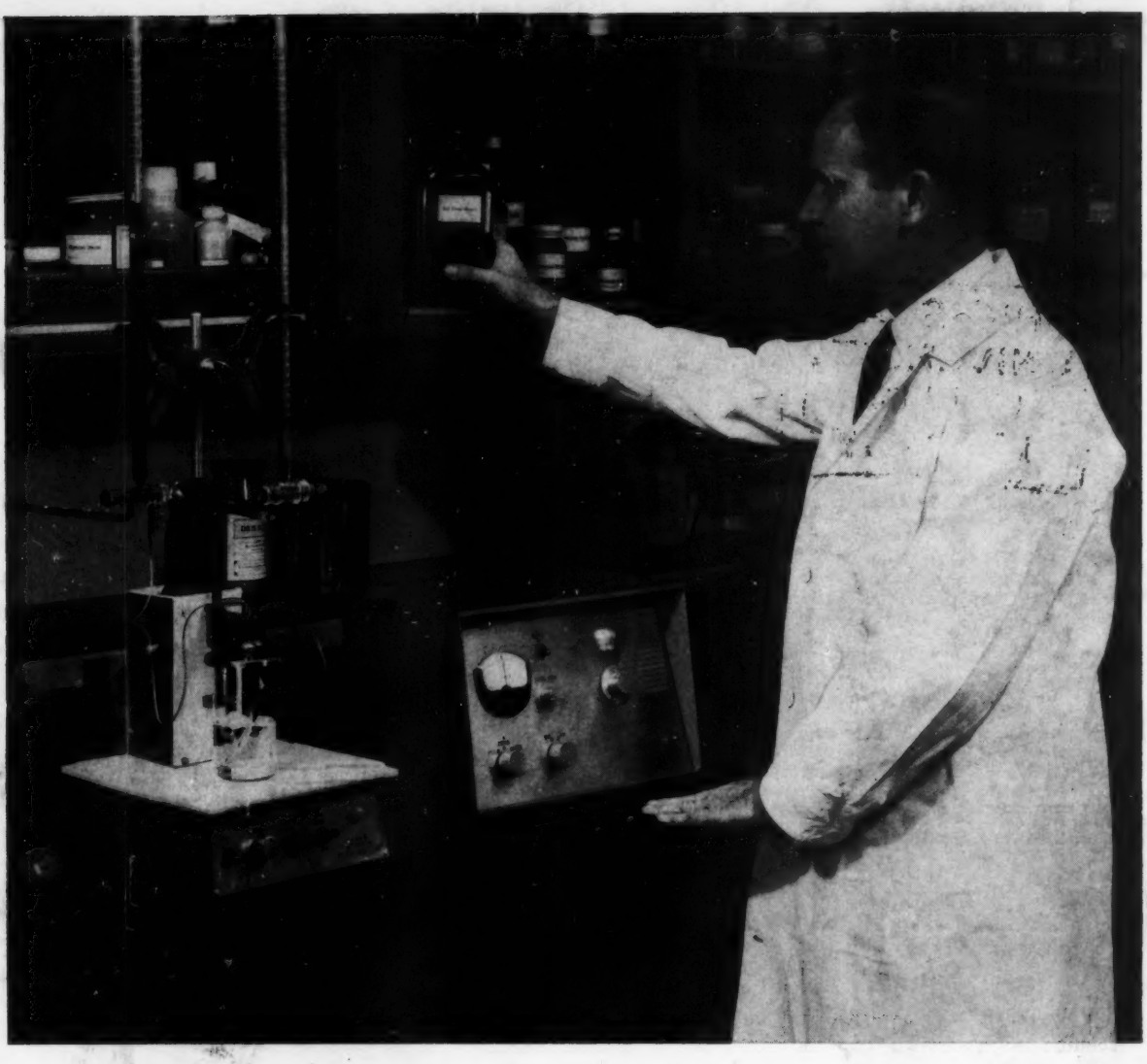

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